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# Probing the ionic structure of FLiNaK–ZrF<sub>4</sub> salt mixtures by solid-state NMR†

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In this study, by applying <sup>19</sup>F, <sup>23</sup>Na and <sup>7</sup>Li high-resolution NMR methods, the evolution of the [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> local ionic structures in FLiNaK–ZrF<sub>4</sub> salt mixtures were elucidated. K<sub>3</sub>ZrF<sub>7</sub>, Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>ZrF<sub>6F<sub>31</sub></sub> crystal phases were identified when the melt salts were being solidified. The distribution of these [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> species was dependent on the content of ZrF<sub>4</sub> in FLiNaK eutectic salts. Moreover, K<sub>3</sub>ZrF<sub>7</sub> phase transition from an orthorhombic lattice into a disordered cubic lattice was clarified, thereby causing dynamics of the coordinated F<sup>-</sup> ions to be reduced and the well-ordered crystal lattices to be destroyed. These mentioned results provide a further insight into the Zr–F based ionic structure and the formation of the disordered Zr–F structure in ZrF<sub>4</sub>-based eutectic salts.

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## 1 Introduction

Fluoride eutectic salts have been studied extensively as a coolant or a fuel salt for nuclear reactor systems due to their ability to act as an effective heat transfer fluid at high temperature and low pressure and based on high radiation flux.<sup>1-4</sup> Specific to the fuel salt, the concentration of free oxygen dianion O<sup>2-</sup> is rigorously regulated to avoid UO<sub>2</sub><sup>5-7</sup> being precipitated. As reported by Oak Ridge National Laboratory (ORNL), the zirconium tetrafluoride (ZrF<sub>4</sub>) can act as the O<sup>2-</sup> absorber additive in fuel salts for removing free O<sup>2-</sup> and avoiding UO<sub>2</sub> being precipitated.<sup>8</sup> However, ZrF<sub>4</sub> exerts a significant coordination effect with fluorine anions to form a series of [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> anions, in which the Zr–F–Zr bridges bond chains or networks. In addition, the competition of F<sup>-</sup> anions with other metal ions will drastically impact the salt properties (*e.g.*, the melt viscosity and thermo-conductivity). Accordingly, the structure study on ZrF<sub>4</sub> containing alkali fluorides is capable of presenting valuable information to support the novel fuel salt design, modeling and composition optimization.

To analyze the local structure and phase transformation of [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> ions in AF–ZrF<sub>4</sub> systems (A = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>), numerous experimental and theoretical studies have been conducted. According to Toth *et al.*,<sup>9</sup> the effects of the ZrF<sub>4</sub> concentration on the local ionic structure in LiF–NaF–ZrF<sub>4</sub> eutectic salt were studied under Raman spectroscopy. Three zirconium-based species, *i.e.*, [ZrF<sub>6</sub>]<sup>2-</sup>, [ZrF<sub>7</sub>]<sup>3-</sup> and [ZrF<sub>8</sub>]<sup>4-</sup>, coexist in the

melts. As reported by Dracopoulos *et al.*,<sup>10</sup> the 6-fold and 7-fold coordinated ionic species could form a series of small chains in KF–ZrF<sub>4</sub> eutectic salt. With the F–Zr–F chains formed, the potential to form disordered network structures was illustrated. However, the specific evolution of the ionic structure and the crystal phase formation have been rarely investigated when complicated FLiNaK–ZrF<sub>4</sub> salts are being solidified, as impacted by the overlapped characteristic signals of the IR or Raman spectroscopy. As compared with other IR or Raman spectroscopy, high-resolution NMR method refers to a powerful method to investigate the local structure of ZrF<sub>4</sub>-based systems.<sup>11-14</sup> The high resolution of the NMR signals and the multiple detectable elements (<sup>7</sup>Li, <sup>19</sup>F, <sup>23</sup>Na) are capable of presenting specific microstructure information of the zirconium ions in complex salt system. For instance, Pauvert *et al.*<sup>15</sup> reported the structural evolution of the free fluoride ions and other Zr–F ions in LiF–ZrF<sub>4</sub> system. When ZrF<sub>4</sub> component tended to increase, the bridged Zr–F structure was certified to form Zr–F–Zr chains based on <sup>19</sup>F NMR method.

In this study, the coordination structure of [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> in FLiNaK–ZrF<sub>4</sub> eutectic salts was investigated specifically with high resolution solid-state NMR method.<sup>16</sup> <sup>7</sup>Li, <sup>19</sup>F and <sup>23</sup>Na NMR spectra were adopted to analyze the chemical environment of zirconium ions, as well as the evolution of the different ionic species. As indicated from the results, K<sub>3</sub>ZrF<sub>7</sub>, Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>ZrF<sub>6F<sub>31</sub></sub> crystal phases were formed when the melt FLiNaK–ZrF<sub>4</sub> salts were being solidified. With the increase in the ZrF<sub>4</sub> concentration, K<sub>3</sub>ZrF<sub>7</sub> phase transition from the crystalline phase into the disordered cubic was characterized, thereby suggesting that the dynamics of the coordinated F<sup>-</sup> ions was reduced, and the well-ordered crystal lattices were destructed. This study helps clarify the Zr–F based ionic structure and the evolution of the [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> species, which is critical to the

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solidification, energy storage and segregation of the  $\text{ZrF}_4$ -based molten salts.

## 2 Experimental method

### 2.1 Samples preparation

The NaF (99.99%), KF (99.99%) and LiF (99.99%) were purchased from Aladdin and dehydrated by heating under vacuum at the temperature of 353 K for one week before use, and  $\text{ZrF}_4$  (99.99%) with a cover wrapped by beeswax from Strem Chemicals, Inc without further purification. The highly-purified LiF–NaF–KF (46.5 : 11.5 : 42 mol%) eutectic salt was supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (inductively coupled plasma optical emission spectroscopy, ICP-OES results were shown in Table S1†), without further purification. Considering the eutectic point of 727 K, the  $(\text{FLiNaK})_{\text{eut}}\text{-ZrF}_4$  eutectic solidification salts with various  $\text{ZrF}_4$  compositions were prepared in a glove box under dried argon by artificially mixing suitable proportions between  $(\text{FLiNaK})_{\text{eut}}$  salt and  $\text{ZrF}_4$  at 923 K for keeping 4 h then that directly cool down to room temperature in the furnace. The related information that the number of kinds of ions and the ratio of  $n(\text{F}^-)$  to  $n(\text{Zr}^{4+})$  in  $\text{FLiNaK-ZrF}_4$  ( $0 \leq X_{\text{ZrF}_4} \leq 18.3$  mol%) systems were shown in Table S2.† The eutectic NaF– $\text{ZrF}_4$  (40.5 mol%) and NaF– $\text{ZrF}_4$  (20 mol%) salts were synthesized by the following: 1 g of salts were weighted by artificially mixing suitable proportions in a nickel crucible, then they were heated to 923 K and 1073 K respectively, and kept for 4 hours. After that, the temperature was directly cooled down to room temperature in the furnace. In order to help the discussion, the chemical shift of major compositions measured in  $^{19}\text{F}$  MAS NMR was summarized in Table S3.†

### 2.2 Solid-state NMR experiments

All of the  $^{19}\text{F}$ ,  $^{23}\text{Na}$  and  $^7\text{Li}$  solid-state NMR experiments were performed on a Bruker Avance NEO 400 WB spectrometer with a magnetic field of 9.4 T, operating at frequencies of 376.61 MHz, 105.87 MHz and 155.55 MHz, respectively. The data was collected using a 3.2 mm double-resonance magic angle spinning (MAS) probe and a 15 kHz spinning rate at room temperature. In order to make quantitative experiments more effectively, the following conditions were set: the recycle delay (d1) were 5000 s, 100 s, 3000 s and the number of scans (ns) were 4, 16, 2 for  $^{19}\text{F}$ ,  $^{23}\text{Na}$  and  $^7\text{Li}$  solid-state NMR experiments respectively. The chemical shifts of  $^{19}\text{F}$ ,  $^{23}\text{Na}$  and  $^7\text{Li}$  were referenced using 1 M  $\text{C}_2\text{H}_4\text{O}_2\text{F}_3\text{N}$  aqueous solution ( $\delta = -74.5$  ppm), 1 M NaCl aqueous solution ( $\delta = 0$  ppm) and 1 M LiCl aqueous solution ( $\delta = 0$  ppm) at room temperature, respectively.

### 2.3 X-ray diffraction measurements

X-ray diffraction was performed at room temperature on a Bruker D8 Advance using  $\text{Cu-K}\alpha$  (1.5406 Å) radiation (40 kV, 20 mA). All samples were mounted on the same sample holder and scanned from  $2\theta = 5^\circ$  to  $90^\circ$  at a speed of  $15^\circ \text{ min}^{-1}$ .

## 3 Results and discussion

### 3.1 Formation of the $\text{K}_3\text{ZrF}_7$ crystal phase in $\text{FLiNaK-ZrF}_4$ eutectic salt

The ionic structure of  $\text{FLiNaK-ZrF}_4$  eutectic salts were firstly studied by comparing with  $\text{FLiNaK}$ . For the investigation of the local structure of the ions,  $^{19}\text{F}$ ,  $^{23}\text{Na}$  and  $^7\text{Li}$  solid-state MAS NMR was performed (Fig. 1). The characteristic signal of  $\text{ZrF}_4$  could not be identified in  $^{19}\text{F}$  NMR spectrum of  $\text{FLiNaK-ZrF}_4$  (3.56 mol%) system (Fig. S1†),<sup>17,18</sup> which demonstrated that no  $\text{ZrF}_4$  crystal phase existed in the eutectic salt samples. Comparing to the pure  $\text{FLiNaK}$  eutectic solidification salt in which the signal of KF, LiF and NaF was located at  $-132.9$  ppm,  $-205.4$  ppm and  $-224.6$  ppm respectively,<sup>19</sup> a novel signal at  $-35.0$  ppm was detected, which complied well with the reported result that has the characteristic signal at  $-34.8$  ppm<sup>20</sup> and the XRD results of the authors (Fig. S2†). Moreover, the intensity of KF tended to decrease, which could be induced by the appearance of the new crystal phase. Given the mentioned analysis, the new crystal phase in  $\text{FLiNaK-ZrF}_4$  eutectic salt was demonstrated as  $\text{K}_3\text{ZrF}_7$  crystals. It was interesting to note that no novel signals were identified in the spectrum of  $^{23}\text{Na}$  NMR and  $^7\text{Li}$  NMR (Fig. 1b and c), thereby suggesting that NaF and LiF were not involved in the complexation with  $\text{ZrF}_4$  in  $\text{FLiNaK-ZrF}_4$  system. Moreover, no major change in the integration of  $^{23}\text{Na}$  NMR and  $^7\text{Li}$  NMR signal of NaF and LiF appeared (Fig. S3 and S4†) when the composition of  $\text{ZrF}_4$  was changing from 0 to 13.6 mol%, indicating that NaF and LiF were not involved in the complexation with  $\text{ZrF}_4$  in  $\text{FLiNaK-ZrF}_4$  ( $X_{\text{ZrF}_4} \leq 13.6$ ) systems.

To explore the formation of the new  $\text{K}_3\text{ZrF}_7$  crystals in depth,  $\text{FLiNaK-ZrF}_4$  salts exhibiting different  $\text{ZrF}_4$  contents were synthesized.  $^{19}\text{F}$  NMR was performed on the mentioned samples to elucidate the variation of different crystals (Fig. S5†), and the integration of the relative intensity of the mentioned crystals was plotted in Fig. 2a.

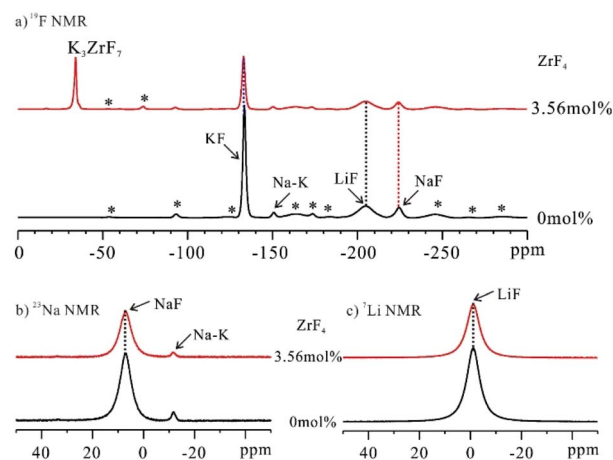


Fig. 1  $^{19}\text{F}$  (a),  $^{23}\text{Na}$  (b) and  $^7\text{Li}$  (c) solid-state MAS NMR spectra of  $\text{FLiNaK}$  eutectic salt (black lines) and  $\text{FLiNaK-ZrF}_4$  (3.56 mol%) eutectic solidification salt (red lines) at ambient temperature. MAS spin rate in the mentioned experiments was set to 15 kHz. Spinning sidebands were marked with asterisks.



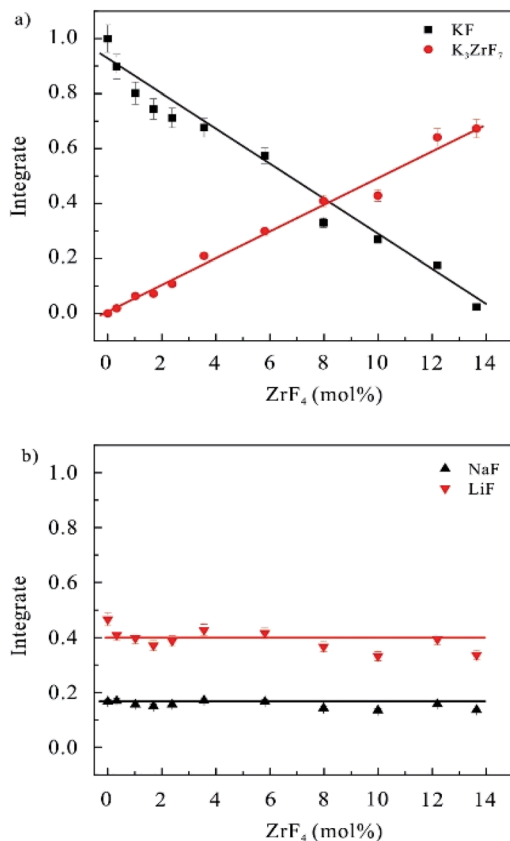


Fig. 2 Integrate of the  $^{19}\text{F}$  NMR signals of different components in FLiNaK– $\text{ZrF}_4$  ( $0 \leq X_{\text{ZrF}_4} \leq 13.6$  mol%) systems versus the molar fraction of  $\text{ZrF}_4$  components.

As the  $\text{ZrF}_4$  contents increased, the number of free fluoride ions  $\text{F}^-$  of  $\text{KF}$  crystal phase declined linearly, while the amount of  $\text{K}_3\text{ZrF}_7$  tended to increase. Under the concentrations of  $\text{ZrF}_4$  reaching 13.6 mol%, the signal of  $\text{KF}$  crystal phase at the  $-132.9$  ppm almost disappeared, and the signal of  $\text{K}_3\text{ZrF}_7$  phase at  $-35.0$  ppm increased to the maximum. Thus, the added  $\text{Zr}^{4+}$  ions were coordinated with the free  $\text{F}^-$  ions, and the  $\text{K}_3\text{ZrF}_7$  crystal phase were formed first when the molten salt was being solidified as impacted by the weaker bonding energy between  $\text{K}^+$  and  $\text{F}^-$  ions than  $\text{Na}^+-\text{F}^-$  and  $\text{Li}^+-\text{F}^-$  ion pairs. Fig. 2b plots the evolving curves of the  $^{19}\text{F}$  NMR signal intensity of  $\text{NaF}$  and  $\text{LiF}$  crystals. No variations of the integration were identified, which suggested that  $\text{NaF}$  and  $\text{LiF}$  crystals existed stably in FLiNaK– $\text{ZrF}_4$  ( $0 \leq X_{\text{ZrF}_4} \leq 13.6$  mol%) salts and were not involved in the complexation with  $\text{ZrF}_4$ . Accordingly, only zirconium-based species  $\text{K}_3\text{ZrF}_7$  was proven to be formed in FLiNaK– $\text{ZrF}_4$  ( $0 \leq X_{\text{ZrF}_4} \leq 13.6$  mol%) solidification salts.

### 3.2 Complexation between $\text{ZrF}_4$ and $\text{NaF}$

Given the mentioned analysis, ionic structure of  $\text{Na}^+$  ions remained unchanged in FLiNaK– $\text{ZrF}_4$  salts with  $\text{ZrF}_4$  concentration less than 13.6 mol%. To study the local ionic structure of  $\text{Na}^+$  ions in FLiNaK– $\text{ZrF}_4$  salts, the  $^{23}\text{Na}$  NMR was performed on the salt samples exhibiting higher  $\text{ZrF}_4$  concentration (Fig. 3).

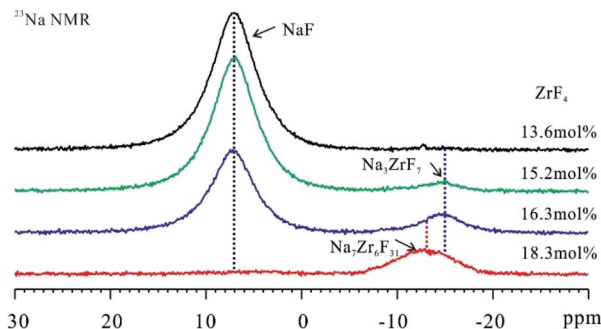


Fig. 3  $^{23}\text{Na}$  NMR spectra of FLiNaK– $\text{ZrF}_4$  ( $13.6 \leq X_{\text{ZrF}_4} \leq 18.3$  mol%) eutectic solidification salts at ambient temperature. MAS spin rate in the mentioned experiments was set to 15 kHz.

The signal of  $\text{NaF}$  at 7.1 ppm tended to decrease and finally disappeared in the spectrum of  $^{23}\text{Na}$  NMR with the rise of the  $\text{ZrF}_4$  content in FLiNaK salt. Moreover, the disappearance of the  $\text{NaF}$  crystal phase was verified according to  $^{19}\text{F}$  NMR results (Fig. S6†). It was therefore revealed that the complexation was developed between  $\text{NaF}$  and  $\text{ZrF}_4$  phases when  $\text{ZrF}_4$  component increased in FLiNaK. In addition, one broad signal at  $-15.0$  ppm presented when 15.2 mol% of  $\text{ZrF}_4$  component was introduced to FLiNaK salt. With the composition of  $\text{ZrF}_4$  increasing further to 16.3 mol%, this signal remained and tended to increase. As suggested from this result, the Na-based coordinated crystal phases were formed in the mentioned salts. With the increase of the  $\text{ZrF}_4$  concentration (18.3 mol%), this signal would shift to the low field ( $-12.9$  ppm) and together with the half-peak width increased. This may be caused by the distribution of different new formed Na-based coordinated crystal phases.

To confirm the ion structure of the mentioned two types of Na-based complexes,  $\text{NaF}-\text{ZrF}_4$  (40.5 mol%) and  $\text{NaF}-\text{ZrF}_4$  (20 mol%) binary systems were prepared for comparison. Fig. 4 illustrates the  $^{23}\text{Na}$  MAS NMR spectra for FLiNaK– $\text{ZrF}_4$  (16.3 mol%) and FLiNaK– $\text{ZrF}_4$  (18.3 mol%) salts. Obviously, one

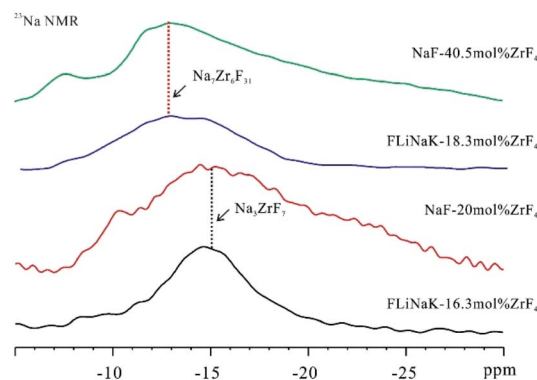


Fig. 4  $^{23}\text{Na}$  solid-state MAS NMR spectra of FLiNaK– $\text{ZrF}_4$  (16.3 mol%) and FLiNaK– $\text{ZrF}_4$  (18.3 mol%) eutectic solidification salt and binary salts like  $\text{NaF}-\text{ZrF}_4$  (20 mol%) and  $\text{NaF}-\text{ZrF}_4$  (40.5 mol%) at ambient temperature. MAS spin rate in the mentioned experiments was set to 15 kHz.



broad peak at  $-15.0$  ppm was present in FLiNaK-ZrF<sub>4</sub> (16.3 mol%) salt.

As inspired by Thoma *et al.*,<sup>21</sup> Na<sub>3</sub>ZrF<sub>7</sub> crystals should exist in NaF-ZrF<sub>4</sub> (20 mol%), so the <sup>23</sup>Na NMR signal at  $-15.0$  ppm belonged to Na<sub>3</sub>ZrF<sub>7</sub> crystal phase. Moreover, a broad signal at nearly  $-12.9$  ppm was identified in NaF-ZrF<sub>4</sub> (40.5 mol%) salt, which was reported to have Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> crystal phase.<sup>21</sup> Thus, the low field shift of the broad signal might be attributed to the formation of Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> crystal phase in FLiNaK-ZrF<sub>4</sub> (18.3 mol%) salt.

### 3.3 Phase transition of K<sub>3</sub>ZrF<sub>7</sub> crystals

With the formation of Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> crystals, a phase transition of K<sub>3</sub>ZrF<sub>7</sub> crystals was also observed with the increase in the ZrF<sub>4</sub> concentration. Fig. 5 presents the <sup>19</sup>F NMR spectra of FLiNaK-ZrF<sub>4</sub> ( $13.6 \leq X_{\text{ZrF}_4} \leq 18.3$  mol%) eutectic salts. Three signals with different full widths at half maximum (FWHM), *i.e.*, F'<sub>1</sub>, F''<sub>1</sub> and F'''<sub>1</sub>, were located at  $-35.0$  ppm,  $-36.9$  ppm and  $-37.8$  ppm in FLiNaK-ZrF<sub>4</sub> (13.6 mol%) system, respectively. With the increase in the concentration of ZrF<sub>4</sub>, the strength of F'<sub>1</sub> site decreased rapidly, and that of F''<sub>1</sub> and F'''<sub>1</sub> sites increased. Moreover, the new F''<sub>1</sub> and F'''<sub>1</sub> signals were observed to be broadened compared with F'<sub>1</sub>. In accordance with the existing reports,<sup>22–24</sup> three crystal phases could exist in K<sub>3</sub>ZrF<sub>7</sub>, *i.e.*, orthorhombic, tetragonal and disordered cubic lattice. Formation of the disordered cubic crystal phase always leads to the reduction of the crystallinity, and the broadening of the NMR signals should originate from the formation of the disordered crystal phase in the eutectic salt. Thus, for the higher ZrF<sub>4</sub> systems, *i.e.*, 16.3 mol% and 18.3 mol% of ZrF<sub>4</sub> within FLiNaK, K<sub>3</sub>ZrF<sub>7</sub> was a disordered cubic crystal. According to the gradual increase of F''<sub>1</sub> and F'''<sub>1</sub> signals and the gradual decrease of F'<sub>1</sub> signals with the increase of ZrF<sub>4</sub> contents, it can be deduced that the K<sub>3</sub>ZrF<sub>7</sub> phase transition was changed from orthorhombic lattice into disordered cubic lattice.

The formation of different [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> ionic structures and crystal phases during the solidification of the salt melts could be discussed. After heating into melts, Zr<sup>4+</sup> ions tended to form a coordinated structure with F<sup>-</sup> ions as [ZrF<sub>7</sub>]<sup>3-</sup> or [ZrF<sub>6</sub>]<sup>2-</sup>, which is similar to the results that [AF<sub>7</sub>]<sup>3-</sup>, [AF<sub>8</sub>]<sup>4-</sup> and [AF<sub>9</sub>]<sup>5-</sup>

coexisted in LiF-AF<sub>4</sub> (A = Th<sup>4+</sup> or U<sup>4+</sup>) molten salt.<sup>25,26</sup> When cooling down, K<sub>3</sub>ZrF<sub>7</sub> crystal phase would be formed first as impacted by the weak bonding energy of K<sup>+</sup> and F<sup>-</sup> ions. The absence of [ZrF<sub>6</sub>]<sup>2-</sup> could be attributed to the instability of such Zr-F coordination in solid phase. With the concentration of ZrF<sub>4</sub> increasing continuously, Na<sup>+</sup> ions would be involved in the formation of the new crystal phases and cause Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> crystal phases to appear. This result was well consistent with the existing results that diffusion coefficients of K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup> successively increased within molten AF-ZrF<sub>4</sub> systems (A<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>).<sup>27</sup> Moreover, the disordered cubic crystal phase of K<sub>3</sub>ZrF<sub>7</sub> was formed as the ZrF<sub>4</sub> contents increased in FLiNaK. The formation of such disordered structure should account for the broadening of the <sup>19</sup>F NMR signals of the characteristic signals of K<sub>3</sub>ZrF<sub>7</sub> in the FLiNaK-ZrF<sub>4</sub> eutectic salts exhibiting higher ZrF<sub>4</sub> concentration.

## 4 Conclusions

In brief, the evolution of the ionic structure of [Zr<sub>x</sub>F<sub>y</sub>]<sup>4x-y</sup> with the increase in ZrF<sub>4</sub> compositions in FLiNaK solidification salts was investigated specifically with NMR method. As indicated from the results, the complexation reactions of ZrF<sub>4</sub> tended to proceed as KF > NaF > LiF. Moreover, the predominant species (*e.g.*, K<sub>3</sub>ZrF<sub>7</sub>, Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub>) were formed, and the distribution of the mentioned species varied with the amount of ZrF<sub>4</sub> compositions from 0 to 18.3 mol%. To begin with, the content of K<sub>3</sub>ZrF<sub>7</sub> was increased to maximum when ZrF<sub>4</sub> content was 13.6 mol%, then gradually decreased. However, the contents of Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> was increased when ZrF<sub>4</sub> contents was more than 13.6 mol%. Moreover, the phase of K<sub>3</sub>ZrF<sub>7</sub> was observed to transit from orthorhombic lattice into disordered cubic lattice in the samples exhibiting higher ZrF<sub>4</sub> concentration, thereby causing the well-ordered crystal lattices to be destructed. The mentioned results present a further insight into the local structure of ZrF<sub>4</sub>-based molten salt and glasses systems.

## Author contributions

Rongshan Lan: investigation; formal analysis; writing – original draft; Yiyang Liu: methodology; Ling Han: ICP-OES measurement analysis; Jing Yang and Huiqin Yin: resources of original materials; Min Ge and Yuan Qian: supervision; Hongtao Liu and Xiaobin Fu: conceptualization; writing – review and editing; funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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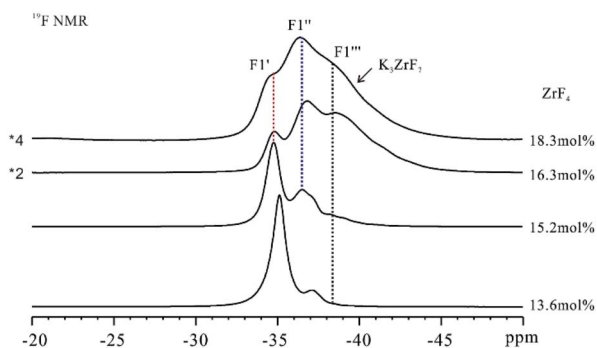


Fig. 5 <sup>19</sup>F NMR spectra of FLiNaK-ZrF<sub>4</sub> ( $13.6 \leq X_{\text{ZrF}_4} \leq 18.3$  mol%) eutectic solidification salts at ambient temperature. MAS spin rate in the mentioned experiments was set to 15 kHz.



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