

## Thermodynamic modeling of LiF-NaF-KF-CrF<sub>3</sub> system

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### ABSTRACT

The thermodynamic evaluation and optimizations of the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> systems were carried out within the framework of CALPHAD (CALCulation of PHase of Diagrams) approach. The liquid phase was described by the associated solution model, and the intermediate phase were treated as stoichiometric compound model. All the model parameters were optimized based on the experimental phase equilibria data from experimental measurements and theoretical predictions (First-principles calculation and empirical equation). A set of self-consistent and reliable thermodynamic parameters was obtained, which can well describe the phase equilibria and thermodynamic properties of the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> system. Furthermore, the database for the LiF-NaF-KF-CrF<sub>3</sub> quaternary system was preliminarily established using Muggianu extrapolation model. Meanwhile, the solubility of CrF<sub>3</sub> in FLiNaK at different temperatures was obtained. The calculated value is in good agreement with the reported measurements by ORNL, considering kinetic factor of K<sub>3</sub>CrF<sub>6</sub> involved in FLiNaK.

### 1. Introduction

Molten salt reactor (MSR), where the fluorides of fissile and/or fertile (such as UF<sub>4</sub>, PuF<sub>3</sub>, ThF<sub>4</sub> and so on) are dissolve in a mixture of molten fluorides, is regarded as one of the six promising candidate reactors for the Generation IV Nuclear Energy System [1–3]. Unlike the conventional “solid” fuel system, MSR has incomparable advantages, such as high negative temperature coefficient of reactivity, inherent safety, very low operate pressure, refueling, processing and fission product removal online, potential unique capabilities and so on [4–6]. Due to the high temperature and very low pressure features of MSR, the reactor core tends to miniaturization and modularization. It can be widely used in nuclear electricity generation, thermochemical hydrogen production [7], oil processing and oil refineries [8], etc.

The mixture of <sup>7</sup>LiF and BeF<sub>2</sub> (mole fraction of LiF-BeF<sub>2</sub>: 0.66–0.34) is a good solvent for fissile and fertile material fluorides [9]. However, FLiBe is extremely poisonous (the maximum permissible concentration of beryllium in working condition is 10<sup>-3</sup> mg/m<sup>3</sup>) [10]. FLiNaK (mole fraction of LiF-NaF-KF: 0.465–0.115–0.42) which has the similar thermo-physical properties as FLiBe [11–13] shown in Table 1, is used as the model of FLiBe during the test stage. It can be learned that the element Cr of nickel-based alloys are corroded easily by fluoride salt compared with other metal elements at high temperature [14–16]. The

complex ions of Cr can be formed which cannot be readily removed due to the intrinsic stability. CrF<sub>3</sub> is the major existing form of chromic fluoride in FLiNaK [11,17]. Although the solubility of CrF<sub>3</sub> in FLiNaK is very important for determining the equilibrium between FLiNaK and nickel-based alloys, there are few related experimental data. The CALPHAD method which is viable in fast obtaining phase equilibria in multicomponent system, is employed to study the solubility and multivariate distribution forms of Cr in FLiNaK melts.

In order to obtain the phase equilibrium and thermodynamic properties of LiF-NaF-KF-CrF<sub>3</sub>, thermodynamic descriptions of each binary subsystem is essential. Thus, this work will give the thermodynamic modeling of the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> binary systems based upon the CALPHAD approach. Within the framework of CALPHAD method, the model parameters are usually optimized in terms of the required phase equilibria and thermochemical information. If lacks of the pertinent measurement, the data from theoretical prediction are sometimes considered for the parameter optimization, such as the first principles calculation is adopted for the prediction of the formation enthalpies of the intermediate compounds KCrF<sub>4</sub>, NaCrF<sub>4</sub>, Na<sub>5</sub>Cr<sub>3</sub>F<sub>14</sub> and Na<sub>3</sub>CrF<sub>6</sub>. Finally, the acquired thermodynamic parameters of these two binary system along with the other subsystems [18–20] are employed to extrapolate into the quaternary LiF-NaF-KF-CrF<sub>3</sub> system for predicting the solubility of CrF<sub>3</sub> and existent forms in FLiNaK melts.

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**Table 1**  
Properties of molten FLiNaK salt and FLiBe at 700 °C [13].

Molten Salt	FLiNaK	FLiBe
Melting point (°C)	454	460
900 °C vapor pressure (mmHg)	0.7	1.2
Density (g/cm <sup>3</sup> )	2.02	1.94
Volumetric heat capacity(cal/cm <sup>3</sup> °C)	0.91	1.12
Thermal conductivity(W/m K)	0.92	1.0

## 2. Data evaluation and prediction

Thermodynamic description of a certain system based on the CALPHAD approach requires the systematical analysis, evaluation and selection of the experimental data from the literature. When experimental measurements are scarce, theoretical predictions are sometimes needed prior to the thermodynamic optimization.

### 2.1. Review of literature information

There are many thermodynamic assessments related to the three systems (LiF-NaF, LiF-KF and NaF-KF) and a very exhaustive review has been processed by Wang [18] in 2013, hence it is not repeated in this work. The results reported by Wang for the LiF-NaF, LiF-KF and NaF-KF binary systems are mainly adopted in our work.

The experimental information concerning phase equilibria and thermochemical data of MF-CrF<sub>3</sub> (M = Li, Na and K) are very limited. Only Kozak et al measured their phase equilibria information in 1969 and 1975, respectively. Recently, thermodynamic assessment of LiF-CrF<sub>3</sub> and KF-CrF<sub>3</sub> have been done in our previous work [19,20] using the associated solution model in liquid phase. Thermodynamic parameters of LiF-CrF<sub>3</sub> from our previous work are adopted in the present work. Here, KF-CrF<sub>3</sub> was reevaluated using a different stoichiometric compounds in liquid phase, compared with our previous work [20]. The literature evaluation of LiF-CrF<sub>3</sub> and KF-CrF<sub>3</sub> has been summarized in refs. [19,20]. Until now, the NaF-CrF<sub>3</sub> system has not been described thermodynamically. The detailed literature evaluation of NaF-CrF<sub>3</sub> system is shown in the following part.

There are two groups of researchers who have measured the experimental phase equilibria of NaF-CrF<sub>3</sub> binary system. In 1969, Kozak et al. [21] firstly determined the phase relations of this system through differential thermal analysis. Again, this binary system was measured by Kozak and Samouel in 1975 [22] aiming at establishing the phase equilibria of the ternary NaF-ZnF<sub>2</sub>-CrF<sub>3</sub> system. However, some disagreements existed in the two reported phase relations of this binary system, where Na<sub>5</sub>Cr<sub>3</sub>F<sub>14</sub> is congruent melting in Ref. [22] and incongruently melting in Ref. [21]. The later measured results are regarded to be more reliable, which are thus adopted for optimization. This system includes three intermediate compounds, namely Na<sub>5</sub>Cr<sub>3</sub>F<sub>14</sub>, Na<sub>3</sub>CrF<sub>6</sub> and NaCrF<sub>4</sub>, which were identified by means of X-ray diffraction (XRD). The whole phase diagram is thus divided into various phase regions featured by one peritectic reaction ( $CrF_3 + liquid \xrightleftharpoons[T=1240.15K]{Per} NaCrF_4$ ) and three eutectic reactions ( $liquid \xrightleftharpoons[T=1133.53K]{Eut} NaCrF_4 + Na_5Cr_3F_{14}$ ,  $liquid \xrightleftharpoons[T=1143.71K]{Eut} Na_3CrF_6 + Na_5Cr_3F_{14}$  and  $liquid \xrightleftharpoons[T=1162.81K]{Eut} Na_3CrF_6 + NaF$ ).

### 2.2. First-principles methodologies

First-principles calculation, based on density functional theory (DFT) can reduce the uncertainties in model parameters of thermodynamic databases, can complement thermodynamic parameter optimization by providing some needed thermochemical data of individual phases with the dearth of relative experimental data [23].

Up to now, the thermochemical information is unavailable on the

**Table 2**  
Single point energy of intermediate compounds in the MF-CrF<sub>3</sub> (M = Li, Na and K) system from First-principles calculation.

Compound	Space group	Single point energy	Resource
LiF	<i>Fm</i> $\bar{3}$ <i>m</i>	−9.7108 eV	[19]
CrF <sub>3</sub>	<i>R</i> $\bar{3}$ <i>cr</i>	−25.6115 eV	[20]
CrF <sub>3</sub>	<i>R</i> $\bar{3}$ <i>ch</i>	−25.6019 eV	[20]
Li <sub>3</sub> CrF <sub>6</sub>	<i>C</i> 12/ <i>C</i> 1	−55.1735 eV	[19]
KF	<i>Fm</i> $\bar{3}$ <i>m</i>	−8.4342 eV	[20]
KF	<i>Pm</i> $\bar{3}$ <i>m</i>	−8.2271 eV	[20]
KCrF <sub>4</sub>	<i>Pnma</i>	−34.6875 eV	[20]
NaF	<i>Fm</i> $\bar{3}$ <i>m</i>	−8.7538 eV	This work
NaCrF <sub>4</sub>	<i>P</i> 21/ <i>C</i>	−34.7474 eV	This work
Na <sub>5</sub> Cr <sub>3</sub> F <sub>14</sub>	<i>P</i> 21/ <i>N</i>	−122.0770 eV	This work
Na <sub>3</sub> CrF <sub>6</sub>	<i>P</i> 21/ <i>C</i>	−52.7634 eV	This work

intermediate compounds of the MF-CrF<sub>3</sub> (M = Na and K) binary system. First-principles calculation is used to predict their formation enthalpies. The following Eq. (1) will show how to obtain the formation enthalpies of the compounds.

$$\Delta_f H_{(MF)_x(CrF_3)_y} = E_{tot}((MF)_x(CrF_3)_y) - xE_{tot}(MF) - yE_{tot}(CrF_3) \quad (1)$$

For the above equations,  $E_{tot}$  is the single point energy of *MF*, *CrF<sub>3</sub>* and  $(MF)_x(CrF_3)_y$  at 0 K listed in Table 2. In fact, CrF<sub>3</sub> has two allotropic forms cited from the Inorganic Crystal Structure Database (ICSD). Here, the more stable form *R* $\bar{3}$ *cr* for CrF<sub>3</sub> is selected to predict the formation enthalpy. The formation enthalpies of intermediate compounds (NaCrF<sub>4</sub>, Na<sub>5</sub>Cr<sub>3</sub>F<sub>14</sub> and Na<sub>3</sub>CrF<sub>6</sub>) in the NaF-CrF<sub>3</sub> binary system are obtained by the following equations. However, only KCrF<sub>4</sub> of the KF-CrF<sub>3</sub> binary system could be calculated by First-principles methodologies (Due to the lack of relative crystal structure information and lattice parameters of K<sub>2</sub>Cr<sub>5</sub>F<sub>17</sub> and K<sub>2</sub>CrF<sub>5</sub>, First-principles calculation failed to be performed on K<sub>2</sub>Cr<sub>5</sub>F<sub>17</sub> and K<sub>2</sub>CrF<sub>5</sub>. What's more, although the crystal structure of K<sub>3</sub>CrF<sub>6</sub> can be known, single point energy of K<sub>3</sub>CrF<sub>6</sub> is not be determined, where the site of F atom is not kept fixed at their static lattice positions [24]).

$$\Delta_f H_{NaCrF_4} = E_{tot}(NaCrF_4) - E_{tot}(NaF) - E_{tot}(CrF_3) \quad (2)$$

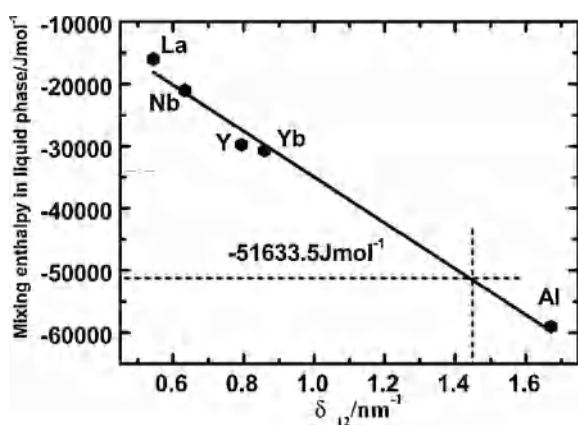
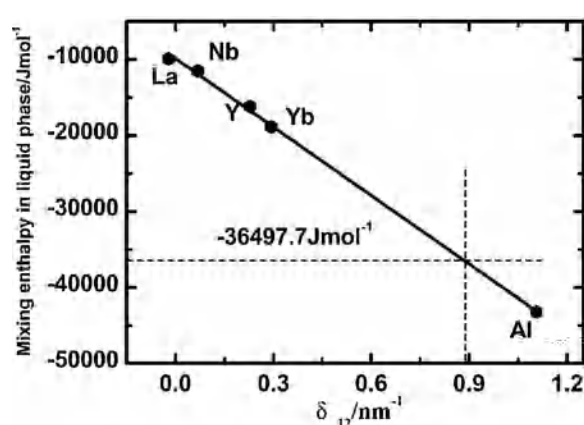
$$\Delta_f H_{Na_5Cr_3F_{14}} = E_{tot}(Na_5Cr_3F_{14}) - 5E_{tot}(NaF) - 3E_{tot}(CrF_3) \quad (3)$$

$$\Delta_f H_{Na_3CrF_6} = E_{tot}(Na_3CrF_6) - 3E_{tot}(NaF) - E_{tot}(CrF_3) \quad (4)$$

The total energies of the compounds in the MF-CrF<sub>3</sub> system were calculated using Vienna ab initio Simulation Package (VASP) [25] based on spin-polarized density function theory (DFT) and generalized gradient approximation (GGA) [26] employed. We used Projector Augmented Wave pseudopotentials (PAW) [27] with the constant energy cutoff of 450 eV for all the calculations to ensure the more accurate results. Extensive tests of k-point calculation indicated that all the energy differences were converged to within 1 meV/atom. Eventually, homologous k-point space mesh can be obtained by means of Monkhorst-Pack scheme with self-consistent iteration convergence threshold of 10<sup>−4</sup> eV, and geometry optimization convergence criteria for all the atomic positions optimized around each atom force was less than 0.02 eV/Å. To validate the rationalization of calculated parameters, the comparisons between before and after structure optimization of cell parameters are shown in Table 3. As seen in Table 3, the relative deviations of all the unit cell lattice constants in NaF-CrF<sub>3</sub> before and after the lattice relaxation are less than 2.1%, and the deviation of the largest volumes are less than 3.1%. Although the first principles calculation is at 0 K, the calculated parameters are reasonable in terms of experimental errors introduced in this paper and the enthalpy of formation independent of temperature.

**Table 3**Comparison of calculated with experimental lattice constants of all compounds included in NaF-CrF<sub>3</sub> and KF-CrF<sub>3</sub> systems (experimental data in Parentheses).

Compound	Space group	Lattice parameters (Å)			Volume (Å <sup>3</sup> cell <sup>-1</sup> )	Resource
		a	b	c		
KF	<i>Fm</i> $\bar{3}$ <i>m</i>	5.4470(5.3670)	5.4470(5.3670)	5.447(5.3670)	161.6570(154.595)	[20]
KF	<i>Pm</i> $\bar{3}$ <i>m</i>	3.2660(3.0600)	3.2660(3.0600)	3.2660(3.0600)	34.8550(28.6530)	[20]
KCrF <sub>4</sub>	<i>Pnma</i>	15.9680(15.73-20)	7.5440(7.4330)	18.6060(18.33-10)	2241.4640(2143.5-500)	[20]
CrF <sub>3</sub>	<i>R</i> $\bar{3}$ <i>cr</i>	5.3170(5.2640)	5.3170(5.2640)	5.3170(5.2640)	97.8440(94.9660)	[20]
CrF <sub>3</sub>	<i>R</i> $\bar{3}$ <i>ch</i>	5.3880(5.2060)	5.3880(5.2060)	5.3880(5.2060)	97.0430(87.5270)	[20]
NaF	<i>Fm</i> $\bar{3}$ <i>m</i>	3.2716(3.2880)	3.2716(3.2880)	3.2716(3.2880)	24.7610(25.1362)	This work
NaCrF <sub>4</sub>	P21/C	7.9013(7.8620)	5.3546(5.3280)	7.4430(7.4060)	308.4174(303.837-0)	This work
Na <sub>5</sub> Cr <sub>3</sub> F <sub>14</sub>	P21/N	10.6147(10.50-96)	7.2975(7.2253)	7.3440(7.2713)	568.8374(552.108-0)	This work
Na <sub>3</sub> CrF <sub>6</sub>	P21/C	5.5187(5.4913)	5.7306(5.7021)	9.7101(9.6618)	251.4889(247.754-0)	This work

**Fig. 1.** The mixing enthalpy of the binary KF-CrF<sub>3</sub> liquid evaluated from the empirical method.**Fig. 2.** The mixing enthalpy of the binary NaF-CrF<sub>3</sub> liquid evaluated from the empirical method.

### 2.3. Empirical prediction for the mixing enthalpy in melts

There are no experimental data for the mixing enthalpy in liquid phase of MF-CrF<sub>3</sub> (M = Na and K) binary systems. Here, an empirical method was applied to estimate them. This method is to build the relation between the mixing enthalpy of binary system and the ionic parameters. As shown in the previous work [28–30], the mixing enthalpy of MF-CrF<sub>3</sub> (M = Na and K) binary system can also be calculated by the following equation,

$$\Delta H_{mix} = f(\delta_{12}) \quad (5)$$

$$\begin{aligned} \delta_{12} &= [(\gamma_M^+ + \gamma_F^-) - (\gamma_{Cr}^{3+} + \gamma_F^-)] / [(\gamma_M^+ + \gamma_F^-)(\gamma_{Cr}^{3+} + \gamma_F^-)] \\ &= [\gamma_M^+ - \gamma_{Cr}^{3+}] / [(\gamma_M^+ + \gamma_F^-)(\gamma_{Cr}^{3+} + \gamma_F^-)] \end{aligned} \quad (6)$$

$\gamma_M^+$  is the ionic radius of M, whose value is referred to an octahedral geometry from the compilation of Shannon [31]. The available cations N<sup>3+</sup> in the present case depend on whether or not there exist enough

measurements for the mixing enthalpy of the MF-NF<sub>3</sub> (M = Na and K) binary system. The experimental mixing enthalpies of the MF-AlF<sub>3</sub>, MF-LaF<sub>3</sub>, MF-YF<sub>3</sub>, MF-NdF<sub>3</sub>, MF-YbF<sub>3</sub> (M = Na and K) [32–34] binary systems were reported, and the datum near the mole fraction of 0.5 mol MF-0.5 mol NF<sub>3</sub> (M = Na and K, N = Al, La, Y, Nd and Yb) were chosen to predict the analytic expression for Eq. (5) after carefully searching the literature. Table 4 lists the ionic radius of all the ions and their values of the parameter  $\delta_{12}$ . Fig. 1 and Fig. 2 reveals the dependence of the mixing enthalpies of various binary systems on their parameters  $\delta_{12}$ , which clearly shows a linear relationship. It should be noted that the mole fraction of 0.5 mol NF<sub>3</sub> was chosen since it corresponds to the approximate composition, where the mixing enthalpy of the liquid in the MF-NF<sub>3</sub> (M = Na and K) binary system is most negative displayed in the reference [32–34]. The mixing enthalpy of 0.5 mol KF-0.5 mol CrF<sub>3</sub> and 0.5 mol NaF-0.5 mol CrF<sub>3</sub> at 1200 K were estimated  $-51633.5 \text{ J mol}^{-1}$  and  $-36497.7 \text{ J mol}^{-1}$ , respectively (Fig. 1 and Fig. 2).

**Table 4**The radius of various ionic and calculated  $\delta_{12}$  for MF-CrF<sub>3</sub> (M = Na and K) binary melts.

ions	La <sup>3+</sup>	Nd <sup>3+</sup>	Y <sup>3+</sup>	Yb <sup>3+</sup>	Al <sup>3+</sup>	Cr <sup>3+</sup>	Na <sup>+</sup>	K <sup>+</sup>	F <sup>-</sup>
Radius(Å)	1.032	0.983	0.900	0.868	0.535	0.615	1.020	1.380	1.330
$\delta_{12}(\text{nm}^{-1})$ - Na <sup>+</sup>	-0.02162	0.06807	0.22899	0.29427	1.10661	0.88607			
$\delta_{12}(\text{nm}^{-1})$ - K <sup>+</sup>	0.54366	0.63335	0.79427	0.85955	1.67189	1.45135			

**Table 5**The lattice stability parameters of MF-CrF<sub>3</sub> (M = Na and K) system.

Compounds	Gibbs Energy/J	Temp./K	Ref.
NaF(Halite)	$-592757.502 + 307.110402T - 53.29914T\ln(T) + 3.451047 \times 10^{-3}T^2 - 2.26795167 \times 10^{-6}T^3 + 248,839.2T^{-1}$	298–1269	[34]
	$-594935.992 + 393.386907T - 64.62899T\ln(T) + 2.769787 \times 10^{-4}T^2 - 1.64256167 \times 10^{-8}T^3 - 4895866T^{-1}$	1269–3500	[34]
NaF(Liquid)	$-559411.002 + 280.8326242T - 53.29914T\ln(T) + 3.451047 \times 10^{-3}T^2 - 2.26795167 \times 10^{-6}T^3 + 248,839.2T^{-1}$	298–1269	[34]
	$-561589.492 + 367.1091292T - 64.62899T\ln(T) + 2.769787 \times 10^{-4}T^2 - 1.64256167 \times 10^{-8}T^3 - 4895866T^{-1}$	1269–3500	[34]
KF (Halite)	$-583869.251 + 257.421863T - 47.79132T\ln(T) - 0.0046140735T^2 - 6.56616 \times 10^{-7}T^3 + 84,928.5T^{-1}$	298–900	[34]
	$-566044.319 + 135.998567T - 32.01124T\ln(T) - 0.005759505T^2 - 1.993335 \times 10^{-6}T^3 - 2839890T^{-1}$	900–1131	[34]
	$-603118.731 + 438.402642T - 71.9648T\ln(T)$	1131–3000	[34]
KF (Liquid)	$-556673.251 + 233.375886T - 47.79132T\ln(T) - 0.0046140735T^2 - 6.56616 \times 10^{-7}T^3 + 84,928.5T^{-1}$	298–900	[34]
	$-538848.319 + 111.95259T - 32.01124T\ln(T) - 0.005759505T^2 - 1.993335 \times 10^{-6}T^3 - 2839890T^{-1}$	900–1131	[34]
	$-575922.731 + 414.356665T - 71.9648T\ln(T)$	1131–3000	[34]
CrF <sub>3</sub> (Halite)	$-1187016.90252566 + 430.727124515671T - 75.9002712554932T\ln(T)$	298–1100	[33]
	$-0.0201758825492859T^2 + 6.91557308038075E - 7T^3 + 392,132.289886474T^{(-1)}$		
	$-1331013.90106899 + 1535.13049498254T - 227.117506286621T\ln(T) + 0.0437786975402832T^2 - 3.39209290822347E-6T^3 + 24,686,955.0628662T^{(-1)}$	1100–1698	[33]
CrF <sub>3</sub> (Liquid)	$-1164040.39856127 + 787.630622067394T - 129.999999038696T\ln(T)$	298–2500	[33]

### 3. Thermodynamic models

#### 3.1. Lattice stabilities

The stable phase of MF (M = Na and K) is  $Fm\bar{3}m$  symmetry, of which melting points are 1130 K (NaF) and 1269 K (KF).  $R\bar{3}cr$  is the stable phase of CrF<sub>3</sub> whose melting point is 1698 K. Their Gibbs energy functions are described as the following Eq. (7), and the pertinent coefficients of CrF<sub>3</sub> and MF (M = Na and K) are listed in Table 5 cited from literature [35] and [36], respectively.

$${}^{\circ}G_i^{\phi}(T) = G_i^{\phi}(T) - H^{SER} = a + bT + cT \ln(T) + dT^2 + eT^3 + \frac{f}{T} + \dots \quad (7)$$

Where the Gibbs energy function of all phases are referred to the mole enthalpy of pure elements in their stable state at 298.15 K, namely  $H^{SER}$  [37], a, b, c, d, e and f are coefficients, T stands for the absolute temperature (K).

#### 3.2. Thermodynamic modeling for intermediate compounds

There are seven intermediate compounds  $(MF)_x(CrF_3)_y$  (M = Na and K) in MF-CrF<sub>3</sub> (M = Na and K) system. They are treated as the stoichiometric compounds due to no evidence of solid solution in these phases. And the Gibbs energy of the intermediate compounds phase are expressed in the following equation.

$$G_{(MF)_x(CrF_3)_y}^{solid} = xG_{MF}^{\circ} + yG_{CrF_3}^{\circ} + \Delta_r H_{(MF)_x(CrF_3)_y}^{\circ} - T\Delta_r S_{(MF)_x(CrF_3)_y}^{\circ} \quad (8)$$

Where  $G_{CrF_3}^{\circ}$  and  $G_{MF}^{\circ}$  are Gibbs energy of pure species CrF<sub>3</sub> and MF.  $\Delta_r H_{(MF)_x(CrF_3)_y}^{\circ}$  and  $\Delta_r S_{(MF)_x(CrF_3)_y}^{\circ}$  represent enthalpy and entropy of formation of the corresponding intermediate compounds  $(MF)_x(CrF_3)_y$ , respectively. As described in Section 2.2,  $\Delta_f H_{(MF)_x(CrF_3)_y}^{\circ}$  can be obtained from First-principle calculation which is taken as the initial value for the subsequent optimization along with the experimental data.

#### 3.3. Thermodynamic modeling for liquid phase

As seen from the experimental phase diagram of the MF-CrF<sub>3</sub> (M = Na and K), the liquidus are extremely steep. According to the thermodynamic principle, the chemical species with short-range ordering, which cannot be well depicted by the simple substitutional solution model, probably exist in the liquid phase. The associated solution model with specific chemical species can reasonably explain the short-range ordering in the liquid phase. Moreover, the associated

solution model has successfully described of the binary systems of LiF-CrF<sub>3</sub> in our previous work [19]. Thus, the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> will be described by the same solution model. K<sub>3</sub>CrF<sub>6</sub> (different from previous assessment where K<sub>3</sub>CrF<sub>6</sub> and KCrF<sub>4</sub> was as the associate species of KF-CrF<sub>3</sub> binary system in liquid phase) and Na<sub>3</sub>CrF<sub>6</sub>, which are the stable species of Cr<sup>3+</sup> in FLiNaK studied by Peng et al [38], are defined the complex species in the liquid phase as well as our previous work [19].

The Gibbs energy of liquid phase is expressed in the following Eq. (9).

$$G_{MF-CrF_3}^{liq} = x_{MF} G_{MF}^{liq} + x_{CrF_3} G_{CrF_3}^{liq} + x_{M_3CrF_6} G_{M_3CrF_6}^{liq} + RT(x_{MF} \ln x_{MF} + x_{CrF_3} \ln x_{CrF_3} + x_{M_3CrF_6} \ln x_{M_3CrF_6}) + \Delta^E G_{ass}^{liq} \quad (M = Na \text{ and } K) \quad (9)$$

Where  $x_{MF}$ ,  $x_{CrF_3}$  and  $x_{M_3CrF_6}$  stand for the mole fraction of corresponding compounds,  $G_{MF}^{liq}$ ,  $G_{CrF_3}^{liq}$  and  $G_{M_3CrF_6}^{liq}$  refer to the Gibbs energy of pure relevant species in the liquid phase.  $G_{M_3CrF_6}^{liq}$  is given in the following Eq. (10).

**Table 6**  
Thermodynamic information and optimization status of MF-CrF<sub>3</sub> (M = Na and K) system.

Binary system	Compound	Thermodynamic model		Resource
		Intermediate compound (MF) <sub>x</sub> (CrF <sub>3</sub> ) <sub>y</sub>	Species distribution in liquid phase (MF) <sub>x</sub> (CrF <sub>3</sub> ) <sub>y</sub>	
KF-CrF <sub>3</sub>	KF		Associated solution model (KF, CrF <sub>3</sub> , KCrF <sub>4</sub> , K <sub>3</sub> CrF <sub>6</sub> )	[20]
	CrF <sub>3</sub>			
	K <sub>2</sub> Cr <sub>5</sub> F <sub>17</sub>	(KF) <sub>2</sub> (CrF <sub>3</sub> ) <sub>5</sub>		
	KCrF <sub>4</sub>	(KF) <sub>1</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	K <sub>2</sub> CrF <sub>5</sub>	(KF) <sub>2</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
KF-CrF <sub>3</sub>	K <sub>3</sub> CrF <sub>6</sub>	(KF) <sub>3</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	KF		Associated solution model (KF, CrF <sub>3</sub> , K <sub>3</sub> CrF <sub>6</sub> )	This work
	CrF <sub>3</sub>			
	K <sub>2</sub> Cr <sub>5</sub> F <sub>17</sub>	(KF) <sub>2</sub> (CrF <sub>3</sub> ) <sub>5</sub>		
	KCrF <sub>4</sub>	(KF) <sub>1</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
NaF-CrF <sub>3</sub>	K <sub>2</sub> CrF <sub>5</sub>	(KF) <sub>2</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	K <sub>3</sub> CrF <sub>6</sub>	(KF) <sub>3</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	NaF		Associated solution model (NaF, CrF <sub>3</sub> , Na <sub>3</sub> CrF <sub>6</sub> )	This work
	CrF <sub>3</sub>			
	Na <sub>5</sub> Cr <sub>3</sub> F <sub>14</sub>	(NaF) <sub>5</sub> (CrF <sub>3</sub> ) <sub>3</sub>		
NaF-CrF <sub>3</sub>	NaCrF <sub>4</sub>	(NaF) <sub>1</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	Na <sub>3</sub> CrF <sub>6</sub>	(NaF) <sub>3</sub> (CrF <sub>3</sub> ) <sub>1</sub>		
	Na <sub>5</sub> Cr <sub>3</sub> F <sub>14</sub>	(NaF) <sub>5</sub> (CrF <sub>3</sub> ) <sub>3</sub>		

$$G_{M_3CrF_6}^{liq} = 3G_{MaF}^{liq} + G_{CrF_3}^{liq} + \Delta H_{M_3CrF_6}^{liq} - T\Delta S_{M_3CrF_6}^{liq} \quad (M = \text{Na and K}) \quad (10)$$

Where  $\Delta H_{M_3CrF_6}^{liq}$  and  $\Delta S_{M_3CrF_6}^{liq}$  are the enthalpy and entropy of formation of  $M_3CrF_6$ .  $\Delta^E G_{ass}^{liq}$  is the excess Gibbs energy defined by the following Eq. (11) cited from Redlich-Kister polynomial [39].

$$\Delta^E G_{ass}^{liq} = x_{CrF_3} x_{M_3CrF_6}^2 L_{x_{CrF_3}, x_{M_3CrF_6}}^{liq} (x_{CrF_3} - x_{M_3CrF_6})^2 + x_{M_3CrF_6} x_{MF}^2 L_{x_{M_3CrF_6}, x_{MF}}^{liq} (x_{M_3CrF_6} - x_{MF})^2 \quad (11)$$

Where  $L_{x_{CrF_3}, x_{M_3CrF_6}}^{liq}$  and  $L_{x_{M_3CrF_6}, x_{MF}}^{liq}$  are the binary interaction parameters for the corresponding species which depend on temperature in the form  $L^{liq} = a_v + b_v T$ . And the detailed optimized status of sub-binary system MF-CrF<sub>3</sub> (M = Li, Na and K) are listed in Table 6.

#### 4. Results and discussion

The parameter optimization was performed in the Pan Optimizer module of CALPHAD software PANDAT using the least squares method. The formation enthalpies of KCrF<sub>4</sub> (-61.823 kJ/mol), NaCrF<sub>4</sub> (-36.796 kJ/mol), Na<sub>5</sub>Cr<sub>3</sub>F<sub>14</sub> (-141.902 kJ/mol) and α-Na<sub>3</sub>CrF<sub>6</sub> (-85.758 kJ/mol) from First-principles calculation, which were as the initial value of thermodynamic modeling, were input to optimize the relevant phase diagrams. Then, the optimization was conducted in a step by step approach and repeated until an excellent agreement with most experimental data points was reached, within the allowable range of experimental errors. After obtaining the thermodynamic database for different phases in the system, phase diagrams were calculated and plotted accordingly in the PanPhaseDiagram module of the same software.

##### 4.1. Binary system MF-CrF<sub>3</sub> (M = K and Na)

The final thermodynamic parameters, which describe the Gibbs energies of all phases in the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> systems, are listed in Table 7. Based upon these parameters, all the calculated phase

Table 7

Thermodynamic parameters optimized in the present work for the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> system.

KF-CrF <sub>3</sub> system	Resource
$Liq G_{K_3CrF_6} = 3G_{KF}^{Liq} + G_{CrF_3}^{Liq} - 77377.7 + 14.5T$	This work
${}^0L_{CrF_3, K_3CrF_6}^{Liq} = -353517 + 25.8T$	This work
${}^1L_{CrF_3, K_3CrF_6}^{Liq} = 40503.2 + 25.0T$	This work
${}^0L_{K_3CrF_6, KF}^{Liq} = -185213 + 24.3T$	This work
${}^1L_{K_3CrF_6, KF}^{Liq} = 39995.9 + 23.3T$	This work
${}^0G_{K_2CrF_6} = 3{}^0G_{KF} + {}^0G_{CrF_3} - 13354 - 24.5T$	This work
${}^0G_{K_2CrF_6} = 2{}^0G_{KF} + {}^0G_{CrF_3} - 103168 - 14.2T$	This work
${}^0G_{KCrF_4} = {}^0G_{KF} + {}^0G_{CrF_3} - 64912.1 - 9.0T$	This work
${}^0G_{K_2Cr_5F_{17}} = 2{}^0G_{KF} + 5{}^0G_{CrF_3} - 148804 - 20.1T$	This work
$Liq G_{\beta-Na_3CrF_6} = 3G_{NaF}^{Liq} + G_{CrF_3}^{Liq} - 138966 + 14.0T$	This work
${}^0L_{CrF_3, \beta-Na_3CrF_6}^{Liq} = -139140 + 25.0T$	This work
${}^1L_{CrF_3, \beta-Na_3CrF_6}^{Liq} = -50488.4 + 21.1T$	This work
${}^0L_{\beta-Na_3CrF_6, NaF}^{Liq} = -50200 + 24.7T$	This work
${}^1L_{\beta-Na_3CrF_6, NaF}^{Liq} = -28848.6 + 25.0T$	This work
${}^0G_{\beta-Na_3CrF_6} = 3{}^0G_{NaF} + {}^0G_{CrF_3} - 96000 - 25T$	This work
${}^0G_{\alpha-Na_3CrF_6} = 3{}^0G_{NaF} + {}^0G_{CrF_3} - 98373.8 - 22.4T$	This work
${}^0G_{Na_5Cr_3F_{14}} = 5{}^0G_{KF} + 3{}^0G_{CrF_3} - 197000 - 30.0T$	This work
${}^0G_{NaCrF_4} = {}^0G_{NaF} + {}^0G_{CrF_3} - 39990 - 9.6T$	This work

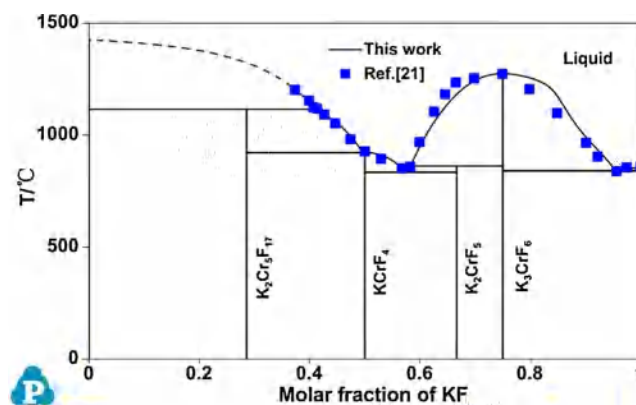


Fig. 3. Calculated phase diagram of KF-CrF<sub>3</sub> along with experiment data.

equilibria and thermodynamic properties together with the related experimental points for the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> systems have been discussed in the following context.

The calculated KF-CrF<sub>3</sub> phase diagram, which covers three eutectic

Table 8

Comparison with calculated values and experimental data of key points in KF-CrF<sub>3</sub> system.

Reaction	Experimental			
	KF/mol%	T/K	KF/mol%	T/K
$K_3CrF_6 \leftrightarrow Liquid$	0.750	1548.15	0.750	1547.88
$K_3CrF_6 + KF \leftrightarrow Liquid$	0.957	1112.04	0.955	1113.30
$K_2Cr_5F_{17} \leftrightarrow Liquid + CrF_3$	0.413	1388.15	0.410	1387.90
$K_2Cr_5F_{17} + KCrF_4 \leftrightarrow Liquid$	0.500	1198.15	0.496	1194.94
$K_2CrF_5 + KCrF_4 \leftrightarrow Liquid$	0.554	1109.26	0.574	1107.09
$K_2CrF_5 \leftrightarrow K_3CrF_6 + Liquid$	0.582	1131.48	0.583	1134.55

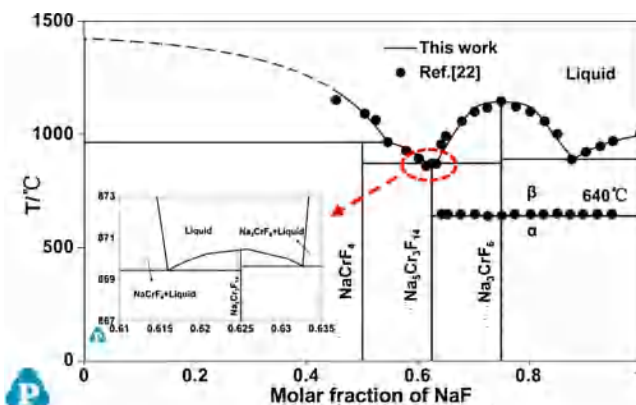


Fig. 4. Calculated phase diagram of NaF-CrF<sub>3</sub> phase diagram along with experiment data.

Table 9

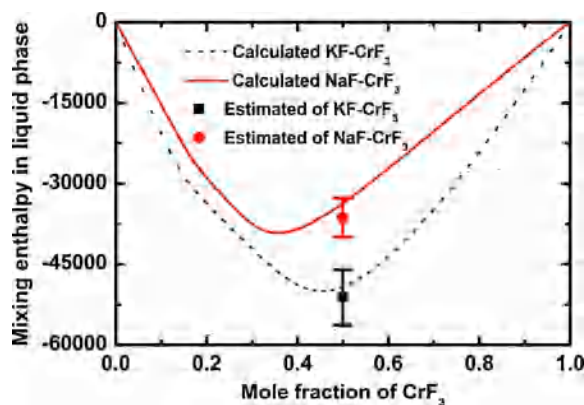
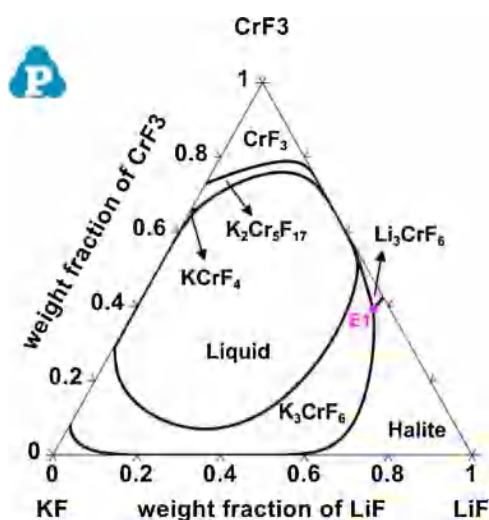
Comparison with calculated values and experimental data of key points in NaF-CrF<sub>3</sub> system.

Reaction	Experimental data		Calculated data	
	NaF/mol%	T/K	NaF/mol%	T/K
$Na_3CrF_6 \leftrightarrow liquid$	0.750	1420.15	0.750	1415.58
$liquid \leftrightarrow Na_3CrF_6 + NaF$	0.877	1162.81	0.886	1162.37
$liquid \leftrightarrow Na_3CrF_6 + Na_5Cr_3F_{14}$	0.633	1143.71	0.626	1142.26
$liquid \leftrightarrow Na_5Cr_3F_{14}$	0.625	1144.85	0.625	1142.27
$liquid \leftrightarrow NaCrF_4 + Na_5Cr_3F_{14}$	0.615	1133.53	0.617	1141.50
$liquid + CrF_3 \leftrightarrow NaCrF_4$	0.546	1239.00	0.548	1237.37

Table 10

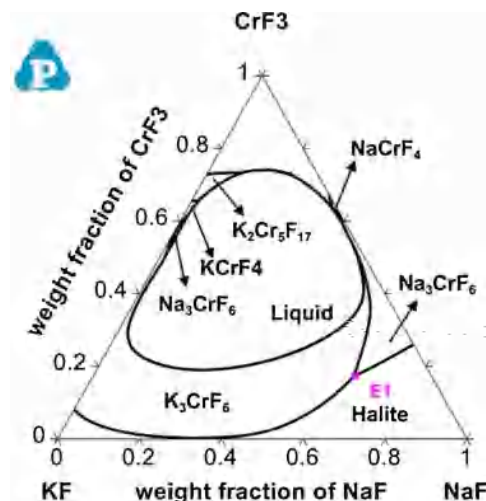
The formation enthalpy of  $\text{KCrF}_4$ ,  $\text{NaCrF}_4$ ,  $\text{Na}_5\text{Cr}_3\text{F}_{14}$  and  $\text{Na}_3\text{CrF}_6$  between First-principles calculation and CALphad method.

Method	$\Delta_f H_{\text{KCrF}_4}^{\text{Solid}}$ (kJ/mol)	$\Delta_f H_{\text{NaCrF}_4}^{\text{Solid}}$ (kJ/mol)	$\Delta_f H_{\text{Na}_5\text{Cr}_3\text{F}_{14}}^{\text{Solid}}$ (kJ/mol)	$\Delta_f H_{\text{Na}_3\text{CrF}_6}^{\text{Solid}}$ (kJ/mol)
First- principles	-61.823	-36.796	-141.902	-85.758
CALPhad	-64.912	-39.990	-197.000	-96.000
Relative deviation	-4.99%	-8.68%	-38.8%	-11.9%

Fig. 5. Calculated mixing enthalpy in liquid phase of  $\text{KF-CrF}_3$  and  $\text{NaF-CrF}_3$  system (1500 °C).Fig. 6. The predicted liquidus projection of the  $\text{LiF-KF-CrF}_3$  system.

and two peritectic reactions, is displayed in Fig. 3 along with the experimental phase equilibria data of Kozak et al. [21]. Table 8 shows the detailed comparison between the calculated and key experimental points. It is clearly manifested from Fig. 3 and Table 8 that the present calculation can well and consistently describe the reported experimental phase equilibria of  $\text{KF-CrF}_3$  system.

Fig. 4 shows the present thermodynamic calculation of the  $\text{NaF-CrF}_3$  system along with experiment data [22], which appears three intermediate compounds, namely  $\text{NaCrF}_4$ ,  $\text{Na}_5\text{Cr}_3\text{F}_{14}$  and  $\text{Na}_3\text{CrF}_6$ . The  $\text{NaCrF}_4$  incongruently melted at the transformation temperature. The latter ones are stable from room temperature to their congruently melting temperature. The enlarged detail of  $\text{Na}_5\text{Cr}_3\text{F}_{14}$  congruently melting part, which contains two eutectic points and one congruent melting point, is shown on the left of phase diagram as seen in Fig. 4. What's more, there is clearly a solid state phase change of  $\text{Na}_3\text{CrF}_6(\alpha - \text{Na}_3\text{CrF}_6 \rightleftharpoons \beta - \text{Na}_3\text{CrF}_6)$  at 640 °C. It can be seen that the calculated results are in excellent agreement with the experimental data points [22], especially the invariant key points. The detail

Fig. 7. The predicted liquidus projection of the  $\text{KF-NaF-CrF}_3$  system.

comparisons between experimental data and calculated results are listed in Table 9.

It can also be manifested from the formation enthalpy of  $\text{KCrF}_4$ ,  $\text{NaCrF}_4$ ,  $\text{Na}_5\text{Cr}_3\text{F}_{14}$  and  $\text{Na}_3\text{CrF}_6$  listed in Table 10 that good consistency exists between First-principles calculation and CALPHAD method, except for the formation enthalpy of  $\text{Na}_5\text{Cr}_3\text{F}_{14}$ . Although there is a larger deviation of formation enthalpy of  $\text{Na}_5\text{Cr}_3\text{F}_{14}$  from two different methods, it should be reasonable considering the First-principles calculation at 0 K within the range of allowable errors.

Fig. 5 shows the calculated mixing enthalpy in the binary  $\text{MF-CrF}_3$  ( $\text{M} = \text{Na}$  and  $\text{K}$ ) systems and the predicted values from the empirical method, respectively. Both of the two curves with V-type characterize the liquid phase with short-range ordering structures. Meanwhile, the calculated mixing enthalpy at the 0.5 molMF–0.5 mol $\text{CrF}_3$  agree well with the estimated values from the empirical method considering the errors.

According to all the figures-tables and related discussions mentioned above, it is suggested that the associated solution model is successfully applied to the  $\text{KF-CrF}_3$  and  $\text{NaF-CrF}_3$  binary systems, where the short range ordering is probably existed in liquid phase. It can be seen that the present thermodynamic parameters are reliable and can well describe the phase equilibrium information of these two systems.

#### 4.2. Ternary systems $\text{LiF-NaF-CrF}_3$ , $\text{LiF-KF-CrF}_3$ and $\text{NaF-KF-CrF}_3$

A series of thermodynamic prediction about thermodynamic properties and phase equilibria of sub-ternary systems were obtained by extrapolation of the relevant binary thermodynamic databases. Figs. 6–8 show the calculated liquidus projections of the  $\text{LiF-NaF-CrF}_3$ ,  $\text{LiF-KF-CrF}_3$  and  $\text{NaF-KF-CrF}_3$ . The calculated main invariant points in these ternary systems are listed in Table 11.

#### 4.3. Prediction of $\text{CrF}_3$ solubility in $\text{FLiNaK}$ molten salt

A set of self-consistent thermodynamic database was derived based on all the binary model parameters ( $\text{LiF-NaF}$ ,  $\text{LiF-KF}$ ,  $\text{NaF-KF}$ ,  $\text{LiF-CrF}_3$ ,

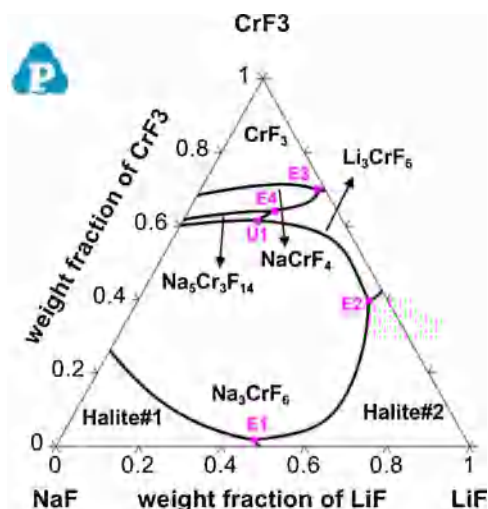


Fig. 8. The predicted liquidus projection of the LiF-NaF-CrF<sub>3</sub> system.

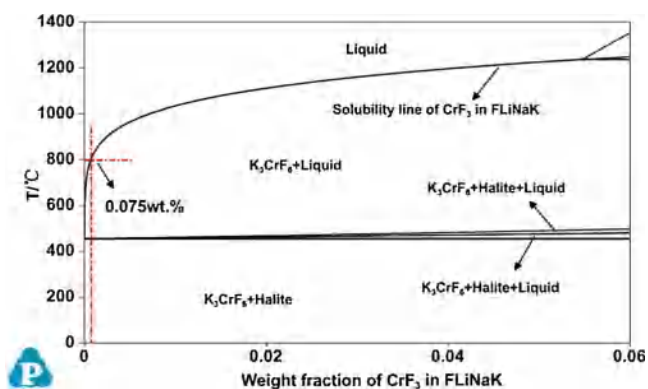


Fig. 9. The solubility of CrF<sub>3</sub> in FLiNaK when the system is under thermodynamic equilibrium.

NaF-CrF<sub>3</sub> and KF-CrF<sub>3</sub>) in order to perform a serial of thermodynamic predictions on the solubility and existence forms of CrF<sub>3</sub> in FLiNaK molten salt. Fig. 9 shows the solubility of CrF<sub>3</sub> in FLiNaK, when the system is under thermodynamic equilibrium. It can be observed that the solubility of CrF<sub>3</sub> in FLiNaK is very low, and is about 0.075 wt.% at 800 °C under thermodynamic equilibrium state.

Fig. 10 shows the solubility of CrF<sub>3</sub> in FLiNaK, when K<sub>3</sub>CrF<sub>6</sub> is negligible in LiF-NaF-KF-CrF<sub>3</sub> system. As observed from Fig. 10, the solubility of CrF<sub>3</sub> in FLiNaK increases dramatically. The solubility of CrF<sub>3</sub> in FLiNaK is about 0.3 wt.% at 600 °C, which is consistent with the reported value reported by ORNL

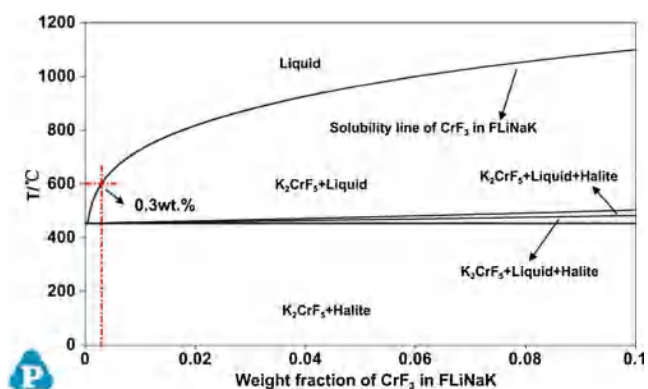


Fig. 10. The solubility of CrF<sub>3</sub> in FLiNaK when K<sub>3</sub>CrF<sub>6</sub> is negligible.

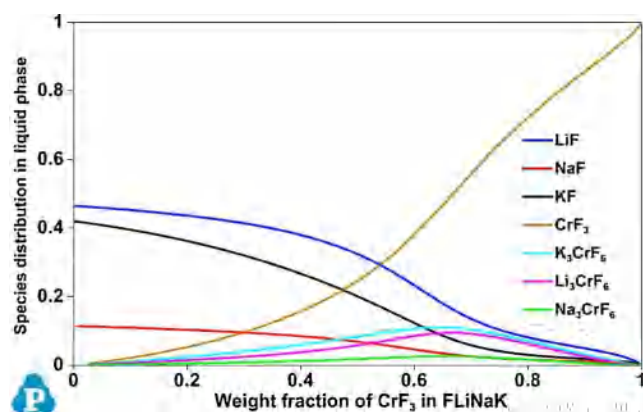


Fig. 11. The species distribution of LiF-NaF-KF-CrF<sub>3</sub> quaternary system in liquid phase (1500 °C).

$(\frac{0.20+0.19+0.23}{3})(Cr)wt. \% \approx 0.43wt. \%$ ) at 600 °C [40]). It can be suggested that kinetics of K<sub>3</sub>CrF<sub>6</sub> is very low to prevent it from separating out. This phenomenon can be explained qualitatively from its drive force (DF). DF is shown in the following Eqs. (12) and (13)

$$\Delta G^{DF} = G_{K_3CrF_6}^{liq} - G_{K_3CrF_6}^{sol} \quad (12)$$

$$G_{K_3CrF_6}^{liq} = G_{K_3CrF_6}^{sol} + RT \ln(r_{K_3CrF_6} y_{K_3CrF_6}) \quad (13)$$

Where  $G_{K_3CrF_6}^{liq}$  and  $G_{K_3CrF_6}^{sol}$  are the Gibbs free energy function in liquid and solid phase, respectively. And  $\Delta G^{DF}$  is the drive force function of K<sub>3</sub>CrF<sub>6</sub> from liquid phase to solid phase.  $G_{K_3CrF_6}^{liq}$ ,  $r_{K_3CrF_6}$  and  $y_{K_3CrF_6}$  refer to the Gibbs free energy function, activity coefficient and relative amount of K<sub>3</sub>CrF<sub>6</sub> in liquid phase.

It can be seen from above equations that the drive force of K<sub>3</sub>CrF<sub>6</sub> in liquid phase is bound up with the relative amount of K<sub>3</sub>CrF<sub>6</sub> in liquid phase. As observed from Fig. 11, the relative amount of K<sub>3</sub>CrF<sub>6</sub> in liquid phase is very low, especially when weight fraction of CrF<sub>3</sub> is less than 20 wt.% in FLiNaK. It can be learned that the drive force is small and the K<sub>3</sub>CrF<sub>6</sub> cannot separate out under this experimental condition. Therefore, the measured solubility of CrF<sub>3</sub> in FLiNaK is much larger than that the values under the thermodynamic equilibrium state.

Based on the model parameters of LiF-NaF-KF-CrF<sub>3</sub> system, solubility of CrF<sub>3</sub> in FLiNaK is calculated considering kinetic factor of K<sub>3</sub>CrF<sub>6</sub>. Fig. 12 shows the fitting result of calculated solubility of CrF<sub>3</sub> in FLiNaK molten salt, and the correlation  $S$  (Solubility, wt. %) = 0.0075 × T(°C) - 4.29 ( $R^2 = 0.92$ ). A complete set of thermodynamic parameters for LiF-NaF-KF-CrF<sub>3</sub> has been established preliminarily, which can predict the solubility of CrF<sub>3</sub> and form structure in FLiNaK during the operation of MSR.

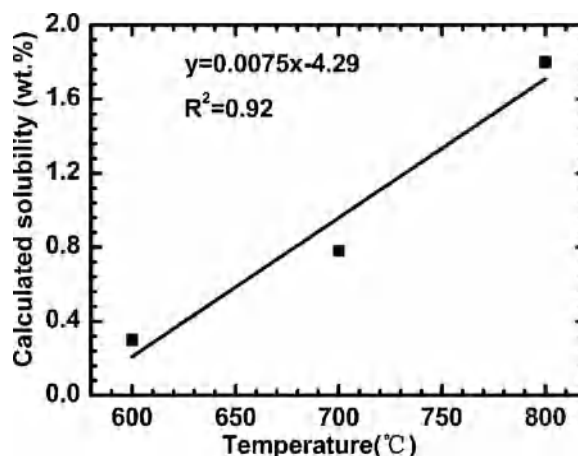


Fig. 12. Calculated solubility of CrF<sub>3</sub> in FLiNaK eutectic and the fitting curve.

**Table 11**  
Invariant points in the LiF-KF-CrF<sub>3</sub>, NaF-KF-CrF<sub>3</sub> and LiF-NaF-CrF<sub>3</sub>.

Ternary system	Reaction type	Temp. (°C)	CrF <sub>3</sub> (wt.)	KF (wt.)	LiF (wt.)
LiF-KF-CrF <sub>3</sub>	$Liquid \xrightarrow{E1} Li_3CrF_6 + K_3CrF_6 + Halite$	719.93	0.39	0.040	0.57
Ternary system	Reaction type	Temp. (°C)	CrF <sub>3</sub> (wt.)	KF (wt.)	NaF (wt.)
NaF-KF-CrF <sub>3</sub>	$Liquid \xrightarrow{E1} Na_3CrF_6 + K_3CrF_6 + Halite$	835.31	0.17	0.64	
Ternary system	Reaction type	Temp. (°C)	CrF <sub>3</sub> (wt.)	LiF (wt.)	NaF (wt.)
LiF-NaF-CrF <sub>3</sub>	$Liquid \xrightarrow{E1} Na_3CrF_6 + Halite\#1 + Halite\#2$	647.530	0.018	0.470	0.512
	$Liquid \xrightarrow{E2} Na_3CrF_6 + Li_3CrF_6 + Halite\#2$	716.540	0.396	0.557	0.047
	$Liquid \xrightarrow{E3} NaCrF_4 + Li_3CrF_6 + CrF_3$	781.430	0.696	0.286	0.018
	$Liquid \xrightarrow{E4} NaCrF_4 + Li_3CrF_6 + Na_5Cr_3F_{14}$	815.90	0.640	0.200	0.160
	$Liquid + Na_3CrF_6 \xrightarrow{U1} Li_3CrF_6 + Na_5Cr_3F_{14}$	828.28	0.620	0.180	0.200

## 5. Conclusions

A complete self-consistent thermodynamic description of the KF-CrF<sub>3</sub> and NaF-CrF<sub>3</sub> system has been obtained based on the CALPHAD method in this work. The associated solution model are successfully applied to describe the liquid phase with short range ordering species. Calculated mixing enthalpy in liquid phase of MF-CrF<sub>3</sub> (M = Na and K) system is consistent with the empirical prediction considering the errors. The formation enthalpy for intermediate phases calculated from CALPHAD method agrees well with the first-principle calculation within the allowable experimental errors.

The thermodynamic parameters of LiF-NaF-KF-CrF<sub>3</sub> system is preliminarily established, based on all the binary subsystems using Muggianu extrapolation. The calculated solubility of CrF<sub>3</sub> in FLiNaK at 600 °C is in good agreement with the measured value by ORNL, and the fitting result of calculated solubility of CrF<sub>3</sub> in FLiNaK with temperature has been obtained considering the dynamic factor of K<sub>3</sub>CrF<sub>6</sub> during the initial stage. This can provide a series of thermodynamic predictions on the phase equilibria and thermodynamic properties in the quaternary LiF-NaF-KF-CrF<sub>3</sub> system, and will also contribute to calculating other salt systems with more components. It can be used to provide guides during the operation of MSR.

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