

## Identification of structural entities in NdF<sub>3</sub>-LiF melts with cryoscopic method

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**Abstract:** Nd-F species in NdF<sub>3</sub>-LiF melts were studied using cryoscopic method. Liquidus temperatures of melts of various compositions were determined by differential thermal analysis(DTA). Based on the different model calculations, NdF<sub>4</sub><sup>−</sup> was identified as the most likely Nd-F entity in the melts in which the mole fraction of NdF<sub>3</sub> was lower than 20%, considering only one single Nd species in the melt, and which was formed in accordance with Temkin model or Flood model. Then, activities of different components in the melts were researched. The results show that activity of LiF decreases, and that of NdF<sub>3</sub> increases with increasing the mole fraction of NdF<sub>3</sub>. The value of activity coefficient of NdF<sub>3</sub> is higher than 1, and that of LiF is lower than 1.

**Key words:** structural entities; NdF<sub>3</sub>-LiF melts; cryoscopic method; liquidus temperature

### 1 Introduction

Electrolysis of fluoride-oxide melts is an important process to produce Nd and Nd-Fe alloys. In this process, NdF<sub>3</sub> acts as the solvent for the oxide, and LiF is a necessary secondary component of the electrolyte. So, it is the most important to understand the information about the ionic structure of NdF<sub>3</sub>-LiF melts. Firstly, change of physicochemical properties of melts is actually determined by its structure, so more reasonable electrolyte composition can be obtained through the melts structure research. Secondly, knowledge of the structural properties of NdF<sub>3</sub>-LiF melts is important to understand the dissolution mechanism of Nd<sub>2</sub>O<sub>3</sub> in the melts and then the Nd and Nd-Fe alloy electrolysis process.

Physicochemical properties of the neodymium electrolysis system melts were widely researched. The researched properties contained viscosity[1], surface tension[2], electrical conductivity[3], dissolution behavior of Nd[4], solubility limit of Nd<sub>2</sub>O<sub>3</sub>[5], and so on. However, the ionic structure study of the melts system was limited. Raman spectrometry was the main

technique used for the published results. In the research of PHOTIADIS et al[6] and DRACOPOULOS et al[7] on NdCl<sub>3</sub>-ACl(A=Li, Na, K or Cs) and LnF<sub>3</sub>-KF (Ln = La, Ce, Nd, Sm, Dy or Yb) binary melts, respectively, octahedral LnCl<sub>6</sub><sup>3−</sup> and LnF<sub>6</sub><sup>3−</sup> were thought to exist in the corresponding melts. But the NdF<sub>3</sub>-LiF system had not been involved in the above research. Then, STEFANIDAKI et al[8] had reported the existence of octahedral NdF<sub>6</sub><sup>3−</sup> complex anions in molten binary NdF<sub>3</sub>-LiF eutectic mixture.

Cryoscopic method is an important thermodynamic method to research structure of melts. HU et al[9] has researched the ionic structure of dilute LiF-NdF<sub>3</sub> melts. But the composition range was relatively small. In the present study, ionic structure of NdF<sub>3</sub>-LiF melts was studied by cryoscopic method in a wide composition range and several reaction models were used for calculation. The most reasonable approach was obtained by comparison by the measured and theoretical values.

### 2 Theoretical base

For a binary mixture, an equation was obtained through thermodynamic derivation, using the Gibbs-

Helmholtz equation:

$$\ln a_1 = -\frac{\Delta H_1^\ominus}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (1)$$

where  $a_1$  is the activity of the solvent in the liquid mixture in equilibrium with its pure solid state;  $\Delta H_1^\ominus$  is the standard molar enthalpy of the solvent in J/mol;  $R$  is the universal gas constant, 8.314 J/mol·K;  $T$  is the liquidus temperature of the molten mixture in K and  $T_0$  is the melting point of the solvent in K.

The binary NdF<sub>3</sub>-LiF phase diagram was characterized by a simple eutectic[10]. For NdF<sub>3</sub>-LiF binary melts, LiF could be regarded as the solvent, so the liquidus temperature of the melts could be decreased because of the concentration changes due to the interaction with the solute, namely NdF<sub>3</sub>. The liquidus temperature of the melts is related to the activity of LiF according to Eq.(1), but the projected activity of LiF varies depending on dissolution models for NdF<sub>3</sub>. So, the most reasonable model could be obtained through comparison of measured and theoretical values of the liquidus temperatures of the melts.

### 3 Experimental

All of chemicals were analytical pure, and were dried before being used by slowly increasing the temperature up to 300 °C so that the moisture could be removed.

Differential thermal analysis (DTA) was used to measure liquidus temperature. A DTA-TG thermal analyzer (SDT 2960, TA Instrument, USA) was used in the experiments. All measurements were carried out in Ar atmosphere.

During the measurements, the sample was heated to about 50 K above literature value for the liquidus temperature[10] and then cooled to the temperature about 50 K below that data at a cooling rate of 5 K/min. When the phase change occurred, there appeared an obvious thermal effect peak on the  $\Delta T$ — $T$  curve of the melts. The starting point of the peak corresponded to the beginning of the phase change, and the corresponding temperature was the liquidus temperature.

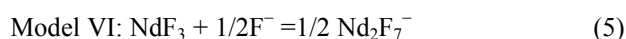
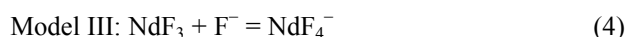
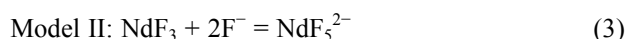
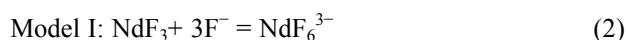
## 4 Results and discussion

### 4.1 Reaction model of NdF<sub>3</sub> in molten LiF

Octahedral NdF<sub>6</sub><sup>3-</sup> complex anion was presented in molten binary NdF<sub>3</sub>-LiF eutectic mixture[8]. The octahedral complex was also proved to exist in a similar melts system, namely AlF<sub>3</sub>-MF (M=Li, Na, K) system which was the basic melts for aluminum electrolysis production[11–12]. Likewise, other two possible kinds of

complex anions were considered in the present study, which were NdF<sub>5</sub><sup>2-</sup> and NdF<sub>4</sub><sup>-</sup>. At last, in our previous work[9], Nd<sub>2</sub>F<sub>7</sub><sup>-</sup> anion was assumed to be a possible existence for dilute NdF<sub>3</sub>-LiF melts in which LiF was the solvent.

It was assumed that Li<sup>+</sup> and F<sup>-</sup> were the only two existing ions in molten LiF. When NdF<sub>3</sub> was added, some reactions would occur between NdF<sub>3</sub> and F<sup>-</sup>. As narrated above, four different reaction models of NdF<sub>3</sub> are as follows.



### 4.2 Calculation of activity of LiF for different models

In the present study, two methods for activity calculation were used. First, Temkin formula[13] was used.

$$a_{\text{LiF}} = x_{\text{Li}^+} x_{\text{F}^-} \quad (6)$$

where  $a_{\text{LiF}}$ ,  $x_{\text{Li}^+}$  and  $x_{\text{F}^-}$  stand for the activity of LiF, mole fractions of Li<sup>+</sup> and mole fraction of F<sup>-</sup>, respectively.

When NdF<sub>3</sub> was added to molten LiF, the mole fraction of different ions would change according to the dissolution reaction models of NdF<sub>3</sub>.

Flood model[13] was another model for calculating LiF activity. In this model, the influence of the electrical charge of ions on mixing entropy of melts was considered based on the Temkin model. In this approach, the activity of LiF was calculated in the same way as that in Temkin model, but the expression of mole fraction of ions was different, as shown in Eq.(7):

$$x_{i^{v-}} = \frac{v n_{i^{v-}}}{\sum_j v_j n_{j^{v-}}} \quad (7)$$

where  $x_{i^{v-}}$  and  $n_{i^{v-}}$  are the mole fraction and mole number of  $i^{v-}$ , respectively;  $n_{j^{v-}}$  is the mole number of  $j^{v-}$ ;  $v$  is the charge number. The mole fraction of the cation is calculated in the same way.

So, when NdF<sub>3</sub> was added to molten LiF, like in Temkin model, the LiF activity for different models could be calculated in Flood model.

In  $N_0$  mol molten LiF, there were  $N_0$  mol F<sup>-</sup>. If  $N_1$  mol NdF<sub>3</sub> was added into the melts, according to calculation equations of the activity for Temkin and Flood models, the expressions of LiF activity for various dissolution models could be obtained, as shown in Table I. What deserves to be mentioned is that the expression of activity for Flood model was the same as that for Temkin model for cases III and IV.

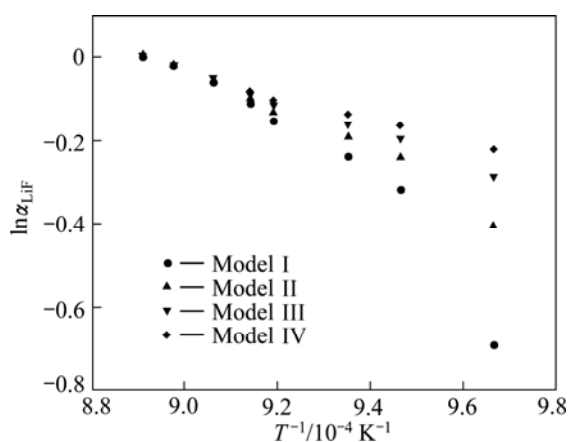
### 4.3 Comparison of various models

If the melts were closed to be in the ideal state, according to Eq.(1), the logarithm of LiF activity was similarly linear to  $1/T$ .

In the present study, the liquidus temperatures of LiF-NdF<sub>3</sub> melts in which mole fractions of NdF<sub>3</sub> were 0, 2%, 5%, 8%, 10%, 13%, 15%, 18% and 20% have been measured, respectively. And then the LiF activity could be calculated using the equations in Table 1. The relationship between values of  $\ln a_{\text{LiF}}$  and  $1/T$  for various NdF<sub>3</sub> dissolution models based on Temkin model and Flood model are shown in Fig.1 and Fig.2, respectively.

**Table 1** Expressions of LiF activity for different dissolution models of NdF<sub>3</sub>

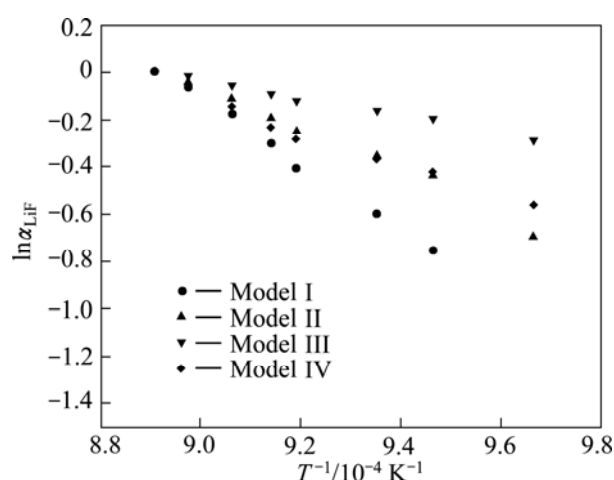
Dissolution model	Expression	
	Temkin model	Flood model
I	$(N_0 - 3N_1)/(N_0 - 2N_1)$	$(N_0 - 3N_1)/N_0$
II	$(N_0 - 2N_1)/(N_0 - N_1)$	$(N_0 - 2N_1)/N_0$
III	$(N_0 - N_1)/N_0$	$(N_0 - N_1)/N_0$
IV	$(N_0 - \frac{1}{2}N_1)/N_0$	$(N_0 - \frac{1}{2}N_1)/N_0$



**Fig.1** Relationship between values of  $\ln a_{\text{LiF}}$  and  $1/T$  of LiF-NdF<sub>3</sub> melts for various NdF<sub>3</sub> dissolution models(based on Temkin model)

Three aspects were considered for determining the most reasonable dissolution model. Firstly, if the deviation between the real melts and the ideal solution was small, the logarithm of LiF activity was similarly linear to  $1/T$ , therefore, if doing linear fit to the various curves in Figs.1 and 2, the smaller the slope deviation was, the higher the linear degree of the corresponding line was, meaning that Temkin or Flood model developed based on assumption of ideal solution was more applicable. Secondly, one could see from Eq.(1) that, the absolute values of the fitted slopes for various curves in Figs.1 and 2 were the ratio of the standard molar enthalpy of LiF and the universal gas constant  $R$ .

Therefore, the values of standard molar enthalpies of LiF for different dissolution models could be obtained through multiplying the absolute values of the fitted slopes of various curves by  $R$ . Then, by comparing the calculated values with the standard value, one could obtain the most reasonable dissolution model. Lastly, from Eq.(1), it could be known that the values of fitted intercepts of the curves in Figs.1 and 2 were the product of the value of the slope and the reciprocal of the melting point of LiF. Therefore, the calculated melting point for different NdF<sub>3</sub> dissolution models could be obtained, and then by comparing the calculated values with the standard value, one could also obtain the most reasonable dissolution model.



**Fig.2** Relationship between values of  $\ln a_{\text{LiF}}$  and  $1/T$  of LiF-NdF<sub>3</sub> melts for various NdF<sub>3</sub> dissolution models(based on Flood model)

The pertinent linear fitting parameters of the different curves in Figs.1 and 2 were shown in Tables 2 and 3, respectively.

Therefore, values of standard molar enthalpies and melting points of LiF for various NdF<sub>3</sub> dissolution models could be calculated using the parameters listed in Tables 2 and 3. The calculated values were shown in Tables 4 and 5. During the calculation, the value of the universal gas constant,  $R$  was taken as 8.314 J/(mol·K).

**Table 2** Pertinent linear fitting parameters of different curves in Fig.1

Model	Slope/K	Slope deviation/ K	Slope deviation rate/%	Intercept
I	8 414.921 67	1 077.415 38	12.803 63	7.560 15
II	5 156.935 07	302.241 4	5.860 87	4.611 62
III	3 726.303 78	122.902 62	3.298 24	3.320 40
IV	1 734.298 41	58.922 23	3.397 57	1.544 06

**Table 3** Pertinent linear fitting parameters of different curves in Fig.2

Dissolution model	Slope/K	Slope deviation/ K	Slope deviation rate/%	Intercept
I	17 298.126	1 434.068 06	8.290 31	15.492 15
II	8 883.273 80	392.766 56	4.421 42	7.932 06
III	3 726.303 78	122.902 62	3.298 24	3.320 40
IV	1 734.298 41	58.922 23	3.397 57	1.544 06

**Table 4** Calculated thermodynamic data of LiF for different  $\text{NdF}_3$  dissolution models based on Temkin model

Dissolution model	$\Delta H_f/(\text{J}\cdot\text{mol}^{-1})$	$T_0/\text{K}$
I	69 961.66	1 113.06
II	42 874.76	1 118.25
III	30 980.49	1 122.25
IV	14 418.96	1 123.21

**Table 5** Values of calculated thermodynamic data of LiF for different  $\text{NdF}_3$  dissolution models based on Flood model

Dissolution model	$\Delta H_f/(\text{J}\cdot\text{mol}^{-1})$	$T_0/\text{K}$
I	143 816.62	1 116.57
II	73 855.54	1 119.92
III	30 980.49	1 122.25
IV	14 418.96	1 123.21

It could be seen through comparison of values of the slope deviation rates in Tables 2 and 3 that for the dissolution models III and IV of  $\text{NdF}_3$  based on the two calculation equations, the values of the slope deviation rates were relatively low, indicating that the linear degree of the corresponding curve was relatively high. This meant that the assumption of ideal solution for the melts was more reasonable according to the existing form of ions and interaction mechanism of the models. Then, by comparing the calculated melting point of LiF with the standard value, 1122K[14], one could find that among the considered models, for model I based on the two calculation equations, the calculated value was far from the standard one, and the differences of the other six models were relatively low. At last, comparison of the calculated molar enthalpies of LiF and the standard one, 27 090 J/mol[14], was made, and it was found that the difference between the calculated values for the model III based on the two calculation equations was relatively low. Therefore, it was thought that the two dissolution modes were more reasonable.

As discussed above, for LiF- $\text{NdF}_3$  melts, in which the mole fraction of  $\text{NdF}_3$  was lower than 20%, the most reasonable dissolution form of  $\text{NdF}_3$  was  $\text{NdF}_4^-$  based on the Temkin or Flood model.

The existence of  $\text{NdF}_4^-$  has not been suggested by other researchers[8]. Furthermore, the mole ratio of LiF to  $\text{NdF}_3$  at the eutectic point of LiF- $\text{NdF}_3$  phase diagram seemed to support the assumption of a presence of  $\text{NdF}_6^{3-}$  species. There may be two reasons for this difference. On the one hand, there may be more than one Nd-F entity in the studied melts, if  $\text{NdF}_6^{3-}$  is assumed to exist in the melts, another entity among the studied models must be  $\text{Nd}_2\text{F}_7^-$ . If in this manner, the situation would become more complex.  $\text{NdF}_5^{2-}$  together with  $\text{Nd}_2\text{F}_7^-$  would also be reasonable. To carry the discussion further, additional new methods would be required. On the other hand, the difference between results of the present study and previously published results might originate from the calculation of the LiF activity in the present study. Both Temkin and Flood models did not consider a mixing heat of melt components. In any event, cryoscopic method had been proved to be valid on NaF- $\text{CaF}_2$ [15] and  $\text{Na}_3\text{AlF}_6$ -LiF[16] melts system.

#### 4.4 Activity of different components in LiF- $\text{NdF}_3$ melts

As mentioned above, in LiF- $\text{NdF}_3$  melts with a  $\text{NdF}_3$  mole fraction lower than 20%,  $\text{Li}^+$  was the only cation, and the anions in the melts were  $\text{F}^-$  and  $\text{NdF}_4^-$ . Thus, the melts could be regard as mixtures of LiF and  $\text{LiNdF}_4$ , and then the activity values of the components corresponding to the Temkin and Flood models could be calculated.

As the ions in the studied melts were all monovalent, the formulas for calculating activity values according to the Temkin and Flood models were the same. Fig.3 showed the calculated activity value together with the mole fraction of the components, as a function of the mole fraction of  $\text{NdF}_3$  in the melts.

It could be seen from Fig.3 that the activity of LiF decreased with increasing mole fraction of  $\text{NdF}_3$ , and that of  $\text{LiNdF}_4$  increased with increasing mole fraction of  $\text{NdF}_3$ . If activity of  $\text{NdF}_3$  in the melts was thought to be the same as that of  $\text{LiNdF}_4$ , it could be seen that when mole fraction of  $\text{NdF}_3$  was low, the activity of components was closed to its mole fraction, and with increasing mole fraction of  $\text{NdF}_3$ , the difference between the activity and mole fraction was more and more obvious.

The activity coefficient was calculated for the components, as shown in Table 6.

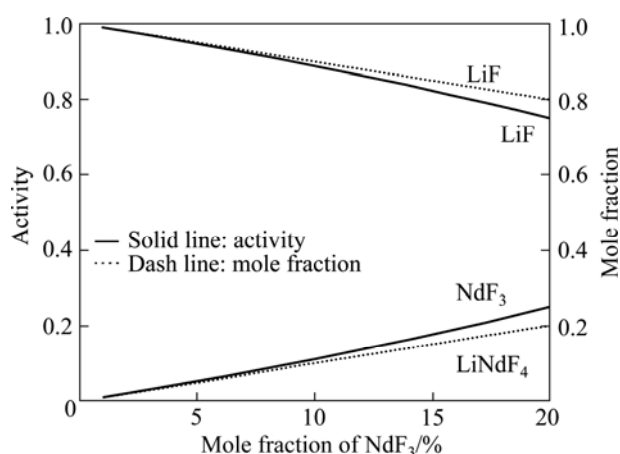


Fig.3 Activity and mole fraction in LiF-NdF<sub>3</sub> melts at 1122 K

Table 6 Activity coefficient of different components in LiF-NdF<sub>3</sub> melts at 1122 K

Mole fraction of NdF <sub>3</sub> /%	Activity coefficient of NdF <sub>3</sub>	Activity coefficient of LiF
0	—	1
2	1.020 4	0.999 6
5	1.052 6	0.997 2
8	1.087 0	0.992 4
10	1.111 1	0.987 7
15	1.176 5	0.968 9
18	1.219 5	0.951 8
20	1.250 0	0.937 5

## 5 Conclusions

1) When NdF<sub>3</sub> is added to molten LiF, it might react with F<sup>-</sup> to form NdF<sub>4</sub><sup>-</sup> (NdF<sub>3</sub> + F<sup>-</sup> = NdF<sub>4</sub><sup>-</sup>), and the ions in the melts are in accordance with Temkin model or Flood model.

2) Activity of LiF decreases with increasing mole fraction of NdF<sub>3</sub>, and that of LiNdF<sub>4</sub> increases with increasing mole fraction of NdF<sub>3</sub>. The value of activity coefficient of NdF<sub>3</sub> is higher than 1, and that of LiF is lower than 1 in the researched mole fraction range of NdF<sub>3</sub>.

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