Study on structural ions of LaF₃-LiF molten salts by cryoscopic method

X P Zhu¹, ², S C Sun¹, ⁴, C Liu¹, G F Tu¹, T Sun² and J Y Zhang³

¹ School of Metallurgy, Northeastern University, Shenyang 110819, China;
² School of Sciences, Northeastern University, Shenyang 110819, China;
³ Shenyang Research Institute of Chemical Industry, Shenyang 110021, China;
⁴ E-mail: neussc@126.com

Abstract. The dynamic thermal analysis method and specially designed experiment device are used to determine the liquidus and solidus temperatures of LaF₃-LiF molten salts in different compositions. Based on the determined results and under the assumed conditions of only one single La species in the molten salts and the formation of the La-F ion in accordance with Temkin or Flood model, the structural ions of LaF₃-LiF molten salts in which the mole fraction of LaF₃ was less than 15% were studied by cryoscopic method. The results show that the most reasonable dissociation reaction mechanism of LaF₃ in LaF₃-LiF melts in which LaF₃ mole fraction is less than 15% is LaF₃+F⁻→LaF₅⁻.

1. Introduction
LaF₃-LiF is the most important electrolyte for producing single rare earth metal lanthanum and its alloys in modern industry. The foundation of developing novel electrolysis technology and equipment are also based on the REF₃-LiF molten salts system. Moreover, REF₃-LiF molten salts are also very significant for their potential use in the extraction of lanthanum (RE) elements from molten salts in the general frame of reprocessing nuclear wastes [1-3]. However, its application has been restricted by a number of issues, such as unclear physicochemical properties. In present years, numerous studies on physicochemical properties of rare earth fluoride electrolytes [4-14] were carried out which were useful for understanding mechanism and process of the electrolysis.

The liquidus temperature of LaF₃-LiF molten salts is a mainstay for choosing reasonable electrolyte composition, energy-saving and cost-reducing of the electrolytic process, which is actually determined by the structural properties. Furthermore, the knowledge of the structural properties of LaF₃-LiF molten salts is helpful to understand the dissolution mechanism of La₂O₃ in the molten salts. The study on ionic structure of the rare earth molten salts is very limited. In the published reports, the molten salts structure was usually studied by Raman spectrum. Photiadis [15] and Dracopoulos [16] have researched on rare earth chlorides and rare earth fluoride binary systems, respectively. They found that RECl₆⁻⁵ and REF₆⁺ existed in the corresponding molten salt system. Stefanidaki et al [17] have reported the existence of NdF₆⁻³ in the binary eutectic mixture molten salt of NdF₃-LiF. Hu [4] thought that NdF₆⁺³ and NdF₄⁻ were both in the binary eutectic mixture molten salts NdF₃-LiF.

Thermodynamic methods are widely used in the study on chemicophysical properties of molten salts [18-23]. The cryoscopic is a significant thermodynamic method to research ions structure of molten salts. The published reports of LaF₃-LiF molten salt system are very limited. Therefore, in this study, liquidus temperature of LaF₃-LiF molten salts with different compositions were measured by...
dynamic thermal analysis and then the structural ions of LaF$_3$-LiF molten salts were studied by cryoscopic method. By comparison the measured values of possible reactions model with theoretical values, the most reasonable reaction and structural ions were obtained.

2. Experimental

All of chemicals were analytically pure. LaF$_3$ and LiF were dried before being used at a temperature of 423 K for 24 hours so that the moisture could be removed. The experimental apparatus mainly consisted of high temperature resistance furnace, temperature sensor and data acquisition system for determination.

In this study, a specially designed novel experimental device is used to determine the liquidus and solidus temperature of rare earth fluoride molten salts, shown in Figure 1. Before the testing step, the rare earth fluoride mixture was heated to a temperature which was about 50 K higher than its liquidus, and then preheated the sampler to the same temperature for the subsequent testing. During the testing, the sample was cooled directly in air and the average cooling rate was about 40 K/ms. A reasonable temperature data acquisition frequency was made in order to obtain accurate testing results, which was set as 50 ms/t in present study. A great number of temperature data were recorded in the computer system after test, and drew the temperature-time curves. Through analyzing the slope changing of these curves, the liquidus and solidus temperature were obtained.

![Figure 1](image-url) Profile of sampling implement-temperature measuring probe.

1-sample container; 2-temperature probe; 3- protective cover; 4-stainless steel carrying rod

3. Results and discussion

3.1. Liquidus temperature of LaF$_3$-LiF molten salts

In the present study, the liquidus and solidus temperature of LaF$_3$-LiF molten salts in which the mole fraction of LaF$_3$ was ranged from 0-40% were tested, the results are shown in Figure 2. It can be seen from Figure 2 that LaF$_3$-LiF system is a simple eutectic in which no intermediate compound formed. The results obtained in this study are consistent with the theoretical phase diagram [24]. The solidus temperature of the binary system is about 1044 K, and it is also quite coincident with the reported value [8].

Based on the experimental data shown in Figure 2, the polynomial fit of the liquidus temperature with the mole fraction of LaF$_3$ were obtained. The fitting polynomials are showing in eq. 1 and eq. 2 which are suitable for different ranges of mole fraction of LaF$_3$ respectively. The fitting parameters showed that the plots have an Adj. R$^2$ with two nines, which shows good reliability equations of these data sets. Thereafter, the fitting polynomials can be used to estimate the liquidus temperature with minimized experimental efforts and at conditions with experiment difficulties.
$T_{\text{Liquidus}}=1222.2221-4.5985x-0.04292x^2$  \hspace{1cm} (1)

$T_{\text{Liquidus}}=749.5664+22.1951x-0.1717x^2$  \hspace{1cm} (2)

Where $T_{\text{Liquidus}}$ is the liquidus temperature of LaF$_3$-LiF system in K; $x$ is the mole fraction of LaF$_3$, mol%. The Eq. 1 is suitable for $x$ range from 0 to 15, and Eq. 2 is suitable for $x$ range from 15 to 40.

It can be seen from the Figure 2 that the system reached the eutectic point when the mole fraction of LaF$_3$ was about 15%. So the liquidus temperature decreased with increasing LaF$_3$ when the mole fraction of LaF$_3$ was less than 15%. Therefore, this study selected the liquidus temperature which the mole fraction of LaF$_3$ was less than 15% as the experimental data to study the structural ions of LaF$_3$-LiF molten salts system by cryoscopic method.

![Figure 2. Phase diagram of LiF-LaF$_3$ molten salts.](image)

3.2. Models for calculation

The liquidus temperature of LaF$_3$-LiF molten salts changes with the changes of concentration of ions, according to the principle of freezing point depression. The activity of LiF was related to the change of the concentration of Li$^+$ and F$^-$ after LaF$_3$ was added to the LiF molten salt, so the liquidus temperature of the system was closely related to the activity of solvent LiF and different dissolution models for LaF$_3$ corresponded to different activities of LiF. It was assumed that four different dissolution models of LaF$_3$ in LiF molten salt were as follows according to the published reports [17, 25-27] on ionic structure of molten salts.

Model I  \hspace{1cm} \text{LaF}_3+3\text{F}^-=\text{LaF}_6^{2-}  \hspace{1cm} (3)

Model II  \hspace{1cm} \text{LaF}_3+2\text{F}^-=\text{LaF}_5^{2-}  \hspace{1cm} (4)

Model III  \hspace{1cm} \text{LaF}_3+\text{F}^-=\text{LaF}_4^-  \hspace{1cm} (5)

Model IV  \hspace{1cm} \text{LaF}_3+1/2\text{F}^-=1/2\text{La}_2\text{F}_7  \hspace{1cm} (6)

The LaF$_3$-LiF molten salts in which the mole fraction of LaF$_3$ was less than 15% could be seen as a dilute solution that LiF was regarded as the solvent, and LaF$_3$ acted as the solute. Based on the thermodynamic derivation, a formula could be deducted from Gibbs-Helmholtz equation for the binary system, shown in Eq. 7.

\[
\ln a_{\text{LiF}}=-\frac{\Delta H_{\text{LiF}}^\theta}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]  \hspace{1cm} (7)

Where $a_{\text{LiF}}$ is the activity of LiF in the molten mixture in equilibrium with its pure solid state; $\Delta H_{\text{LiF}}^\theta$ is the standard molar enthalpy of LiF in J/mol; $R$ is the universal gas constant, 8.314 mol/K; $T_1$ is the liquidus temperature of the molten salts in K and $T_2$ is the melting point of LiF in K.

Temkin model and Flood model were widely used to calculate the activity which were also used in this study. The formula of Temkin model for LiF activity calculation is shown in Eq. 8.

\[
a_{\text{LiF}} = \chi_{L^+} \chi_{F^-}
\]  \hspace{1cm} (8)
Where $\chi_{i}$ and $\chi_{j}$ are the mole concentration of Li$^{+}$ and F$^{-}$ in the molten salts, respectively.

Depending on the different dissolution reaction model of LaF$_3$ in molten LiF, the mole fractions of various ions might be different and the activity of LiF might be different.

Flood model was another method for activity calculation. In this model, the effect of the electrical charge of ions on mixing entropy was considered. So the expression of mole fraction of ions was different from the Temkin model which are shown in Eq. 9 and Eq. 10.

$$\sum \nu \chi_{i}^{\nu} = \sum \nu n_{i}^{\nu} \tag{9}$$

$$\sum \nu \chi_{j}^{\nu} = \sum \nu n_{j}^{\nu} \tag{10}$$

Where $\chi_{i}$, $\chi_{j}$, $n_{i}$, and $n_{j}$ are the mole fraction and mole number of $i^{\nu}$ and $j^{\nu}$, respectively; $\nu$ is the electrical charge of ions. Different activities of LiF were calculated according to the different dissolution reaction models of LaF$_3$ as in Temkin model.

Different expressions of LiF activity were obtained by using the two calculation methods based on different dissolution reaction model of LaF$_3$, which are shown in Table 1.

| Dissolution model | Expression of $a_{LiF}$ |
|-------------------|------------------------|
| Temkin model      | (N$_1$-3N$_2$) / (N$_1$-2N$_2$) |
| Flood model       | (N$_1$-3N$_2$) / N$_1$ |
| (N$_1$-2N$_2$) / (N$_1$-N$_2$) |
| (N$_1$-N$_2$) / N$_1$ |
| (N$_1$-1/2N$_2$) / N$_1$ |

$^a$N$_1$, N$_2$ are the mole number of LiF and LaF$_3$ respectively.

3.3. Comparison of various models

If LaF$_3$-LiF molten salts in which the mole fraction of LaF$_3$ was less than 15% were approximately considered as the ideal solution in which LiF was the solvent, and LaF$_3$ was the solute, the logarithm of LiF activity was similarly linear to the reciprocal of liquidus temperature ($1/T_1$), according to Eq.7. Based on the measured values of liquidus temperature $T_1$ in this study, the $a_{LiF}$ was calculated by the expressions in Table 1, and the relationship between values of $\ln a_{LiF}$ and $1/T_1$ for various dissolution models are shown in Figure 3 and Figure 4.
The most applicable dissolution reaction model of LaF$_3$ can be determined from three aspects. Firstly, based on Eq. 7, the value of logarithm of LiF activity was similarly linear to $1/T_1$ when the real molten salts can be considered as ideal solution. It is necessary to do linear fitting of the various curves in Figures 3 and 4. When the adjusted coefficient $R^2$ was closer to 1, the higher the linear degree of the corresponding line was. At the same time, it also indicated that Temkin or Flood models developed based on assumption of ideal solution was more applicable. Secondly, one could see from Eq. 7 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. And then the most reasonable LaF$_3$ dissolution model could be determined by comparing the calculated values with the standard values. Finally, it also could be seen from Eq. 7 that the values of fitted intercepts of the curves in Figures 3 and 4 were the product of the values of the slopes and the reciprocal of the melting point of LiF. Therefore, the calculated melting point for different LaF$_3$ dissolution models could be obtained, and then the most reasonable dissolution model also could be obtained by comparing the calculated values with the standard value. By means of the above knowledge, the linear fitting parameters of the different curves in Figures 3 and 4 were respectively listed in Table 2 and Table 3 for comparison.

### Table 2. Linear fitting parameters of different curves in Figure 3.

| Dissolution model | Absolute value of slope / K | Adj.$R^2$ | Intercept |
|-------------------|----------------------------|------------|-----------|
| I                 | 4786.97                    | 0.96       | 4.291     |
| II                | 3677.87                    | 0.991      | 3.291     |
| III               | 2879.76                    | 0.998      | 2.567     |
| IV                | 1371.12                    | 0.999      | 1.221     |

### Table 3. Linear fitting parameters of different curves in Figure 4.

| Dissolution model | Absolute value of slope / K | Adj.$R^2$ | Intercept |
|-------------------|----------------------------|------------|-----------|
| I                 | 11528.23                   | 0.988      | 10.32     |
| II                | 6572.83                    | 0.995      | 5.872     |
| III               | 2879.76                    | 0.998      | 2.567     |
| IV                | 1371.12                    | 0.999      | 1.221     |
The calculated values of melting point and standard molar enthalpies of LiF for various LaF₃ dissolution models using parameters in Table 2 and Table 3 are listed in Table 4 and Table 5. The value of \( R \) is taken as 8.314 J/(mol·K).

Table 4. Calculated thermodynamic data of LiF based on Temkin model.

| Dissolution model | \( \Delta H^0_{\text{LiF}} \) (J/mol) | \( T_2 \)/K |
|-------------------|--------------------------------------|-------------|
| I                 | 39798.87                             | 1115.584    |
| II                | 30577.81                             | 1117.554    |
| III               | 23942.32                             | 1121.839    |
| IV                | 11399.49                             | 1122.948    |

Table 5. Calculated thermodynamic data of LiF based on Flood model.

| Dissolution model | \( \Delta H^0_{\text{LiF}} \) (J/mol) | \( T_2 \)/K |
|-------------------|--------------------------------------|-------------|
| I                 | 95845.7                              | 1117.077    |
| II                | 54646.51                             | 1119.351    |
| III               | 23942.32                             | 1121.839    |
| IV                | 11399.49                             | 1122.948    |

By comparing the data listed in Table 2 and Table 3, it can be seen that the values of the adjusted coefficient \( R^2 \) for dissolution models III and IV which no matter calculated by Temkin model or Flood model are closer to 1. It means that the linear degree of the corresponding linear equations are very high which are also more representative. So, the existing form of ions and interaction mechanism of the models III and IV were more applicable based on the theoretical assumption of ideal solution for the molten salts. Then, the calculated melting point of LiF (\( T_2 \)) for dissolution models III and IV whether calculated by Temkin model or Flood model are closer to the standard value, 1122 K [28], this also suggests that the linear regression equations for models III and IV are more representative. Lastly, to compare the calculated molar enthalpies of LiF (listed in Table 4 and Table 5) with the standard one (27090 J/mol) [28], it can be seen that the value for dissolution model III is related to the true one. Therefore, the dissolution model III was considered as more reasonable than others of the four models.

Based on the above discussions, according to the analysis of Temkin and Flood models, in the LaF₃-LiF molten salts in which the mole fraction of LaF₃ was less than 15%, the most reasonable dissolution mechanism for LaF₃ was LaF₃+F⁻=LaF₄⁻. So, the anions were F⁻ and LaF₄⁻, and Li⁺ was the only cation in LaF₃-LiF molten salts. This study on ionic structure was based on the calculation of LiF activity in the molten salts system and the results of this study may be different from the previous publications. Whether Temkin model or Flood model were both established under assumptions, and there must have been some deviations to the real situation. In order to get more reasonable and accurate results, other advanced technologies are needed.

4. Conclusions

(1) Liquidus temperature of LaF₃-LiF melts (mole fraction of LaF₃ were 0~40%) were measured. It was shown that LaF₃-LiF system is a simple binary system without intermediate compound formed. The solidus temperature of the binary molten salts is about 1044K. When reached the eutectic point, the mole fraction of LaF₃ is about 15%.

(2) The reasonable structural ions in the LaF₃-LiF melts were obtained. When LaF₃ is added to LiF molten salt, it might react with F⁻ and to form LaF₄⁻. So, in the LaF₃-LiF melts, the anions are F⁻ and LaF₄⁻, and Li⁺ is the only cation, and the ions are in accordance with Temkin model or Flood model.

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