



# Surface tension of light rare earth fluoride molten salts electrolyte system



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## ABSTRACT

The surface tensions of REF<sub>3</sub>-LiF (RE = La and Nd) molten salts (REF<sub>3</sub> mol% = 20–40%) were measured using the slide method over the temperature range 1223–1423 K which was specifically chosen for meeting the actual electrolysis temperature (about 1323 K). The temperature and composition dependences of the surface tensions were investigated. The results showed that the surface tension decreased linearly with the increasing of temperature and increased nonlinearly with the increasing mole fraction of REF<sub>3</sub>. At 1323 K (near the practical electrolysis temperature), the surface tension of REF<sub>3</sub>-LiF-RE<sub>2</sub>O<sub>3</sub> molten salts firstly increased with the increasing RE<sub>2</sub>O<sub>3</sub> and reached the maximum value near the solubility of RE<sub>2</sub>O<sub>3</sub> (2–3 g) in REF<sub>3</sub>-LiF molten salts, and then decreased with the continuously adding RE<sub>2</sub>O<sub>3</sub>. The accurate knowledge of the surface tension factor of RE<sub>2</sub>O<sub>3</sub> can be useful for well understanding the solubilizing mechanisms of RE<sub>2</sub>O<sub>3</sub> in REF<sub>3</sub>-LiF molten salts system. Results of this study well supplemented the experimental data of physicochemical property on surface tension of rare earth fluoride electrolytes.

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## 1. Introduction

REF<sub>3</sub>-LiF-RE<sub>2</sub>O<sub>3</sub> is the most important electrolyte for producing rare earth metal and its alloys in modern industry [1–4]. In the electrolysis process, REF<sub>3</sub>-LiF molten salts act as the solvent, RE<sub>2</sub>O<sub>3</sub> is the solute which is added continuously because of the consumption. Moreover, REF<sub>3</sub>-LiF molten salts are also very significant for their potential use in the extraction lanthanum (RE) elements from molten salts in the general frame of reprocessing nuclear wastes [5–7]. However, its potential application has been restricted by a number of issues, such as unclear physicochemical properties.

In recently years, the physicochemical properties of rare earth fluoride electrolytes were widely studied, density [8–11], viscosity [12], surface tension [8,13], liquidus temperature [14,15], conductivity [8,16], and the solubility [8,16–18] were included. However, the previous research results did not satisfy the requirements in theoretical research and production application, especially lacking of the reports about basis data on surface tensions. The surface tensions are technologically important parameter in molten salt

electrolysis process. On the one hand, surface tension is one of the key factors for choosing a suitable composition of the electrolyte. On the other hand, the knowledge of surface tension is helpful to understand the interaction among compositions in the molten salts. However, researchers usually study surface tension of high temperature molten salt by estimating models to avoid the difficulties in experimental measurement [19–25]. Although sufficient and continuous data can be obtained by this method, its reliability needs to be verified by experimental determining.

The objective of this research is to find an applicable method for obtaining reliable data about REF<sub>3</sub>-LiF-RE<sub>2</sub>O<sub>3</sub> molten salt's surface tensions. Although the surface tension could be determined by many methods [26–37], it's hard to find applicable one for REF<sub>3</sub>-LiF-RE<sub>2</sub>O<sub>3</sub> melts for the high temperature and strongly corrosive. By the previous studies [38], the slide method was selected to determine the surface tension of REF<sub>3</sub>-LiF-RE<sub>2</sub>O<sub>3</sub> molten salts in this paper. The temperature and composition dependences of the surface tension were investigated systematically.

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**Table 1**  
Experimental reagents.<sup>a</sup>

Reagents	Purity (wt%)	Manufacturer
LaF <sub>3</sub>	>99%	Grrem Advanced Materials Co.,Ltd.
NdF <sub>3</sub>	>99%	Grrem Advanced Materials Co.,Ltd.
La <sub>2</sub> O <sub>3</sub>	>99%	Grrem Advanced Materials Co.,Ltd.
Nd <sub>2</sub> O <sub>3</sub>	>99%	Grrem Advanced Materials Co.,Ltd.
LiF	>99%	Sinopharm Chemical Reagent Co.,Ltd.
NaF	>99%	Sinopharm Chemical Reagent Co.,Ltd.
KCl	>99%	Sinopharm Chemical Reagent Co.,Ltd.

<sup>a</sup> All chemicals are standard reagents and purity stated by manufacturers.

## 2. Experimental procedures

### 2.1. Experiment preparation

All of chemicals were analytical pure (Table 1), RE<sub>2</sub>F<sub>3</sub>, LiF and RE<sub>2</sub>O<sub>3</sub> (RE = La and Nd) were dried before being used under the temperature of 150 °C for 24 h so that the moisture could be removed. Then the RE<sub>2</sub>F<sub>3</sub>-LiF samples in which the mole fraction of RE<sub>2</sub>F<sub>3</sub> was ranged 20–40% were prepared. Because of the strongly corrosive of the high temperature melts, the crucible was made of high-purity graphite material and the specially designed wire and cylinder were made of platinum material. The high-purity argon was also needed to be put into the furnace to protect the equipment from oxidation.

### 2.2. Measurement method

The surface tension was measured using the slide method [8,13,38] which was similar to the detachment methods used by other researchers [35,39]. The slide method involves measuring the maximum downward pull force ( $W_{\max}$ ) necessary to detach the cylinder from the surface of molten salt and determining the other related parameters, then calculating the surface tension by the Eq. (1) [38].

$$\gamma = \frac{(W_{\max} - W_0) \times g}{4\pi R} \times f \quad (1)$$

where the  $W_{\max}$  is the maximum mass in the process of detaching;  $W_0$ , the mass of cylinder in the air;  $R$ , the radius of the cylinder at room temperature;  $g$ , the gravitational acceleration;  $f$ , the correction factor.

In the practically determining process reported in this paper, the constants were calibrated as instrument constant  $K$  except mass using the known surface tension values of molten salt NaCl [40], and the reliability was verified using the known surface tension values of molten salts NaF and KCl. The error analysis in Table 2 indicated that the method was reliable.

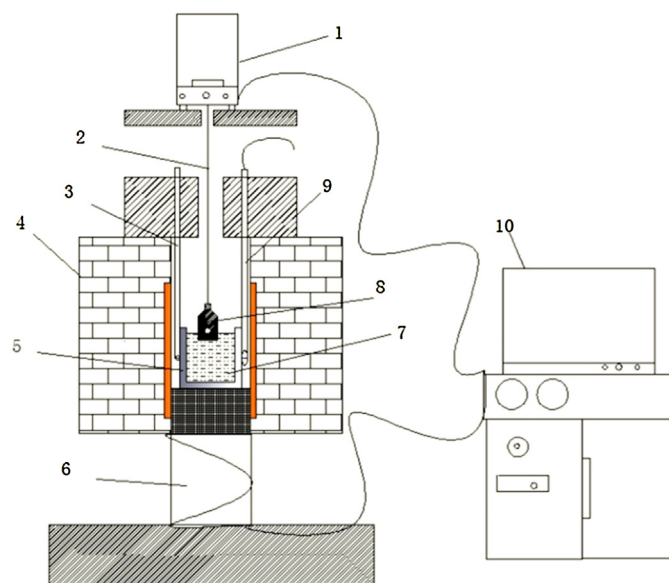
Then the simplification of Eq. (1) can be described as Eq. (2):

$$\gamma = K \times (W_{\max} - W_0) \quad (2)$$

The experimental device (type CM-1 comprehensive testing device for molten salts) and its details were shown in Fig. 1, which was designed and developed by Northeastern University of China.

The sample was melted and then maintained at the desired temperature (about 1 h) until it reached thermal equilibrium before starting measurement. Then the testing software was on and the position of furnace was controlled accurately by the computer system so that the Pt cylinder contacted or detached the surface of molten salt automatically. At the same time, the experimental data was collected and recorded by computer, and by inputting the instrument constant  $K$ , the values of surface tension were obtained.

The overall error in this measurement method was estimated to be within 1.0% of the surface tension value. The standard deviation of the mean (SDOM) for the eight repeated load measurements was 1.25, which corresponded to 0.49% of the surface tension. The



**Fig. 1.** Experimental device for measuring surface tension of molten salts. 1-Electronic balance; 2-Pt wire; 3-Argon inlet; 4-High temperature furnace; 5-High pure graphite crucible; 6-Displacement controller; 7-Molten salts; 8-Pt cylinder; 9-Thermocouple for temperature control; 10-Computer system.

**Table 3**  
Surface tensions of LaF<sub>3</sub>-LiF molten salts,  $\gamma/10^{-3} \text{ N m}^{-1}$  ( $p = 100 \text{ kPa}$ ).<sup>a</sup>

T/K	Mole fractions of LaF <sub>3</sub> (%)				
	20.0	25.0	30.0	35.0	40.0
1223.0	257.3	264.7	272.2		
1248.0	254.9	262.1	269.5		
1273.0	251.8	259	267.2		
1298.0	249.3	256.3	264.9	274.2	
1323.0	247	253.6	262.1	271.4	281.7
1348.0	244.4	251.2	258.9	268.3	279.1
1373.0	242.1	248.8	256.5	265	276.5
1398.0	239.2	246.7	253.8	262.2	274
1423.0	236.9	243.9	251.3	259.8	270.9

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.2 \text{ K}$ ,  $u(p) = 0.7 \text{ kPa}$ ,  $u(x) = 0.1\%$  ( $x$  is the mole fractions of LaF<sub>3</sub>) and the combined expanded uncertainty  $U_c(\gamma) = 0.9 \text{ mN m}^{-1}$  (0.95 level of confidence).

results of error analysis were shown that the slide method for determining the surface tension of RE<sub>2</sub>F<sub>3</sub>-LiF-Re<sub>2</sub>O<sub>3</sub> molten salts was applicable and reliable.

## 3. Results and discussion

### 3.1. Surface tension of RE<sub>2</sub>F<sub>3</sub>-LiF molten salts

One of the explicit objective of this research was determining the surface tensions of RE<sub>2</sub>F<sub>3</sub>-LiF (RE = La and Nd) molten salts by experiment. Then the surface tension of RE<sub>2</sub>F<sub>3</sub>-LiF molten salts for different compositions and temperatures could be obtained by analyzing the amount of data which were obtained from repeated experiments.

The surface tensions of RE<sub>2</sub>F<sub>3</sub>-LiF (RE = La and Nd) molten salts (mol% RE<sub>2</sub>F<sub>3</sub> = 20–40%) were determined and the values of LaF<sub>3</sub>-LiF and NdF<sub>3</sub>-LiF were 236.9–281.7  $\text{mN m}^{-1}$  and 230.8–284.1  $\text{mN m}^{-1}$  which were listed in Tables 3 and 4, respectively. The testing temperatures were 1223–1423 K which was specifically chosen for meeting the actual electrolysis temperature (about 1323 K). And due to the liquidus temperature of LaF<sub>3</sub>-LiF molten salts in which the mole fraction of LaF<sub>3</sub> were 35% and 40% was higher than 1273 K and 1298 K respectively, the measured values corresponded the

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