

SOLUBILITY OF RARE EARTH OXIDES IN MOLTEN FLUORIDES

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Abstract

The limited solubility of rare earth oxides (REOs) in fluoride melt has been an obstacle to preparation of rare earth metals (REMs) by oxide-fluoride electrolysis. However, very little work has been performed in this field. This paper presents a comprehensive analysis of the available data from previous publications. It reveals that the REO solubility increases with temperature and a linear relationship is obtained between the natural logarithm of the solubility and the reciprocal of the absolute temperature. The rare earth fluoride (RF_3) is crucial to REO dissolution and higher solubility is expected in melts with higher RF_3 content. The alkali fluoride (AF) can lower the melting points of binary systems and improve their electrical conductivity. The alkali earth fluoride (AF_2) can further lower the melting points and improve the stability of the melts.

Introduction

Thanks to the unique physical and chemical properties, rare earth elements are widely used in materials and consumer products, and their essential application in permanent magnets, lamp phosphors, rechargeable NiMH batteries has built a tight link to our modern life ¹.

The first attempt to prepare rare earth metals by electrolysis of a oxide-fluoride bath was as early as 1907 ². This was followed by many other investigations owing to the advantages of the process: low cost, environment-friendliness and easier handleability. The solubility of rare earth oxide in fluorides and in-depth understanding of the dissolution behaviour are both of fundamental and engineering importance for the design of electrolyte compositions and process operation. Unlike extensive studies on Al_2O_3 -cryolite system ³⁻⁵, little work has been done for REO-fluoride melts. Even worse, there is inconsistency between results from different studies. This makes the access to reliable data more difficult.

Table 1 lists the major previous studies on solubility of rare earth oxides in molten fluorides. In the present paper, the data from these studies are summarised, reconstructed and analysed systematically for a better understanding of the influence of temperature and melt components on REO solubility in fluoride melts.

Table 1 Investigations on the solubility of rare earth oxides in fluoride melts

Year	REO	Melt	Temperature, K	Solubility, mol. %	Reference
1961	La ₂ O ₃	LiF(-BaF ₂)-LaF ₃	1223	0.61 - 0.78	Porter, 1961 ⁶
1987	Nd ₂ O ₃	LiF-NdF ₃ -MF ₂ (M = Mg, Ca, Ba)	1273	0.14 - 0.96	Du, 1987 ⁷
1991	Nd ₂ O ₃	LiF-BaF ₂ -NdF ₃	1073 - 1173	1.7 - 2.6	Wu, 1991 ⁸
1994	Y ₂ O ₃	LiF-YF ₃	998 - 1273	0.26 - 2.1	Reddy, 1994 ⁹
2002	Nd ₂ O ₃	LiF-NdF ₃ -MgF ₂	1023 - 1173	0.08 - 0.38	Stefanidaki, 2002 ¹⁰
2008	Nd ₂ O ₃	LiF-NdF ₃	1323 - 1423	1.0 - 2.0	Hu, 2008 ¹¹
2012	La ₂ O ₃ , Sm ₂ O ₃ , Ho ₂ O ₃	LiF/NaF/KF-ZrF ₄	873 - 1073	0.039 - 0.73	Pshenichny, 2012 ¹²

Influence of different factors

Temperature

Temperature is an unavoidable factor in studying a thermodynamic property. Figure 1 a shows the dependence of the REO solubility in fluoride melts on the temperature. It is clear that the REO solubility increases with the increase in temperature.

The dissolution of REOs into fluoride melts can be simplified as an endothermal reaction



The equilibrium moving to the right is favoured at higher temperature and consequently higher solubility of rare earth oxides is obtained in the melts.

In Figure 1 b, the natural logarithm of the REO solubility in fluoride melts is plotted against the reciprocal of the absolute temperature for the same data as Figure 1a. It is obvious that most of the data can be interpreted by a linear relationship

$$\ln S_{\text{REO}} = a \times \frac{1}{T} + b \quad (1)$$

where S_{REO} is the REO solubility in mol.% and T the temperature in K.

For example, the solubility of La₂O₃ in 51LiF-49ZrF₄ can be described using eq. (1) with $a = -(5.4 \pm 0.2) \times 10^3$ K and $b = 4.5 \pm 0.2$, with $R^2 = 0.992$, in the temperature range of 873 - 1073 K.

The fitting parameters for the rest of the systems are given in Table 2. Most of the plots have a R^2 with more than two nines, showing good linearity for these data sets. Meanwhile, the differences among the slopes and intercepts indicate the thermodynamic diversity of these systems. The parameters for the linear regression equation are exclusive to that specific system and it is not possible to extend them to an unknown system for solubility estimation. Nevertheless, these parameters are helpful for a more detailed study on thermodynamic features of the systems.

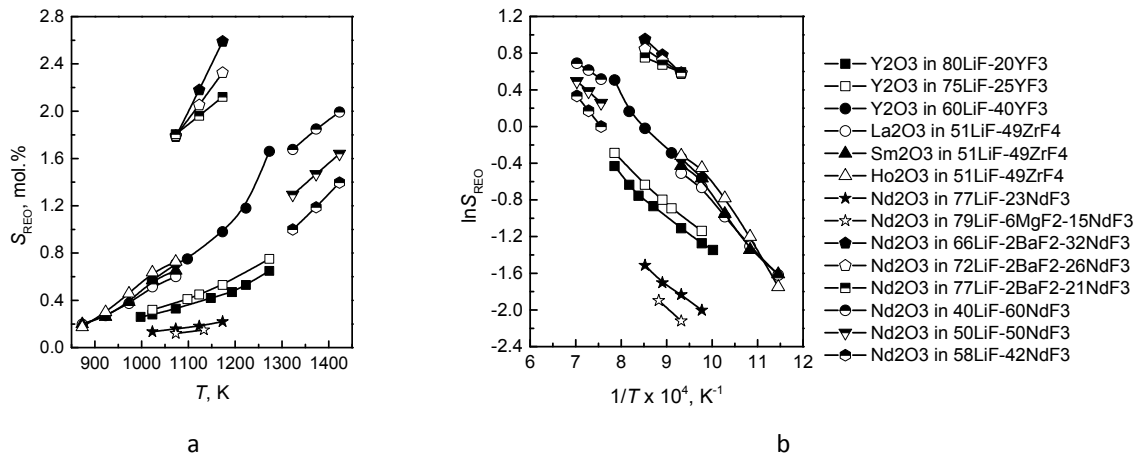


Figure 1 Solubility of rare-earth oxides in fluoride melts as a function of temperature (reproduced with data from reference 7 - 12)

Rare earth fluoride (RF₃) content

Usually, a fluoride melt used to dissolve a rare earth oxide consists of the corresponding rare earth fluoride, an alkali metal fluoride, and sometimes an alkali earth metal fluoride, e.g. Nd₂O₃ in NdF₃-LiF-BaF₂. The RF₃ content, thus, is another essential factor to be considered.

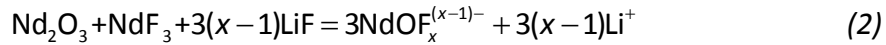
Figure 2 shows the solubility of rare-earth oxides in fluoride melts as a function of rare earth fluoride content. Most of the published data give the same conclusion that the REO solubility increases with the RF₃ content in the melts except a set of data from Wu's study⁸. As his work involved a ternary system, this disagreement could be attributed to the influence from BaF₂.

Table 2 Linear fitting parameters for data plots in Figure 1 (b)

System	R ²	a [10 ³ K]	b
Y ₂ O ₃ in 80LiF-20YF ₃	0.986	-4.1 ± 0.2	2.7 ± 0.2
Y ₂ O ₃ in 75LiF-25YF ₃	0.991	-4.4 ± 0.2	3.2 ± 0.2
Y ₂ O ₃ in 60LiF-40YF ₃	0.960	-5.2 ± 0.5	4.5 ± 0.4
La ₂ O ₃ in 51LiF-49ZrF ₄	0.993	-5.4 ± 0.2	4.5 ± 0.2
Sm ₂ O ₃ in 51LiF-49ZrF ₄	0.980	-5.9 ± 0.4	5.1 ± 0.4
Ho ₂ O ₃ in 51LiF-49ZrF ₄	0.969	-6.8 ± 0.6	6.2 ± 0.6
Nd ₂ O ₃ in 77LiF-23NdF ₃	0.987	-3.8 ± 0.2	1.7 ± 0.2
Nd ₂ O ₃ in 79LiF-6MgF ₂ -15NdF ₃ *	--	-4.5213	2.093
Nd ₂ O ₃ in 66LiF-2BaF ₂ -32NdF ₃	0.999	-4.69 ± 0.08	4.96 ± 0.07
Nd ₂ O ₃ in 72LiF-2BaF ₂ -26NdF ₃	1.000	-3.27 ± 0.01	3.63 ± 0.01
Nd ₂ O ₃ in 77LiF-2BaF ₂ -21NdF ₃	1.000	-2.03 ± 0.02	2.48 ± 0.02
Nd ₂ O ₃ in 40LiF-60NdF ₃	0.994	-3.3 ± 0.2	3.0 ± 0.1
Nd ₂ O ₃ in 50LiF-50NdF ₃	0.999	-4.47 ± 0.08	3.64 ± 0.06
Nd ₂ O ₃ in 58LiF-42NdF ₃	1.000	-6.29 ± 0.02	4.75 ± 0.01

* with only two data

Based on the study of Raman spectra of $\text{NdF}_3\text{-LiF-Nd}_2\text{O}_3$ system, Stefanidaki proposed a reaction between Nd_2O_3 and the molten $\text{NdF}_3\text{-LiF}$ ¹⁰:



This reaction shows that LiF acts only as a F^- ion donor, and that Nd^{3+} can support the REO dissolution process. He also pointed out that the most reasonable candidates of Nd-O-F complex seem to be NdOF_4^{3-} and NdOF_5^{4-} among the mononuclear compounds and $\text{Nd}_2\text{OF}_{10}^{6-}$ and $\text{Nd}_2\text{OF}_8^{4-}$ among the binuclear complexes ¹⁰.

Hu described the Nd_2O_3 dissolution in the melt as a process in which the long-range order in Nd_2O_3 is destroyed by the interaction between O^{2-} and ion complex NdF_6^{3-} and NdF_4 to form NdOF_5^{4-} or $\text{Nd}_2\text{OF}_{10}^{6-}$ ¹¹. Although the formula of the complexes is not exactly the same as Stefanidaki's, his finding confirmed the important role of NdF_3 content in Nd_2O_3 dissolution into molten LiF- NdF_3 . The Nd-F ion complex increases with the content of NdF_3 in the binary system, which is beneficial to Nd_2O_3 dissolution ^{11, 13}.

Similar interaction of oxygen ions with RE-F complexes is expected in other REO-fluoride systems, resulting in a positive influence of RF_3 content on REO dissolution.

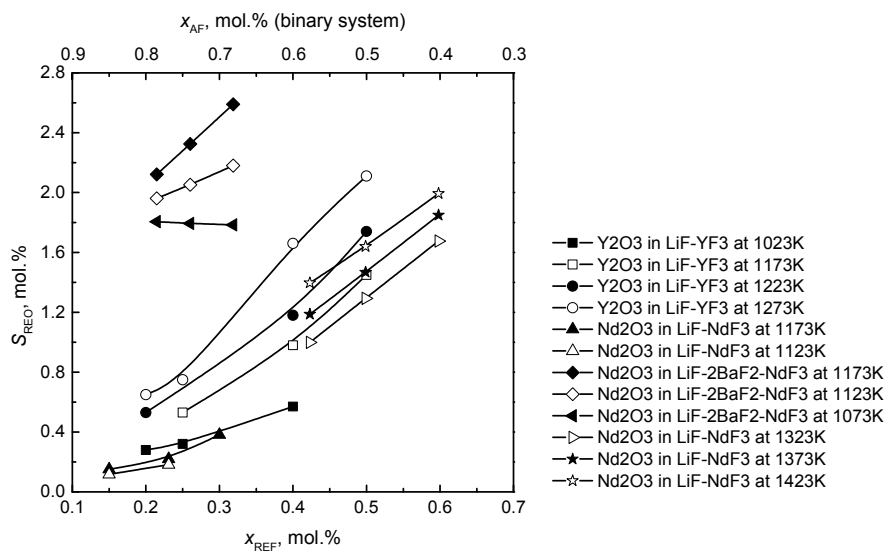


Figure 2 Solubility of rare-earth oxides in fluoride melts as a function of rare earth fluoride content (reproduced with data from reference 8 - 11)

Alkali metal fluoride (AF) content

The main purposes of an alkali metal fluoride addition are to lower the melting point of the electrolyte and improve the electrical conductivity.

The melting points of rare earth fluorides are all higher than 1400 K. Those of light lanthanide fluorides, the main elements prepared by molten salt electrolysis, are even as high as 1650 - 1766 K (see Table 3). However, the cell operation temperature is usually below 1400 K to secure smooth production and good quality and yield of final products. The addition of LiF

can significantly lower the melting points of the melts. The eutectic points are 19 - 27 mol. % RF_3 (around 70 wt. %) and around 1000 K (see Table 3). The addition of NaF and KF can lower the melting points of the binary systems as well ¹⁴.

A study from Hu showed that the electrical conductivity of NdF_3 -LiF melts increased with temperature and the LiF content ¹⁵⁻¹⁶. The radius of Li^+ ion is much smaller than the other cations, resulting in lower resistance of its movement and higher mobility in the melt. Therefore, the conductivity is closely linked to the speed of Li^+ ions and the obstruction of such complexes as NdF_6^{3-} and NdF_4^- to their movement under electric field. It is easy to figure out that the melts with the higher concentration of Li^+ ions and less complex NdF_6^{3-} and NdF_4^- would have higher conductivity.

Table 3 Melting point of RF_3 and eutectic temperature of RF_3 -LiF binary systems

Fluoride	YF3	LaF3	CeF3	PrF3	NdF3	SmF3	GdF3	DyF3
Melting point *, K	1421	1766	1710	1672	1650	1579	1504	1427
Eutectic temperature (RF_3 -LiF) **, K	968	1043	1028	1023	1011	971	973	973

* data from reference 17

** data from reference 14

Since higher REO solubility can be obtained in melts with higher RF_3 content, the AF content in a binary melt ($x_{\text{AF}} = 1 - x_{\text{RF}_3}$) should have a negative effect (see Figure 2).

Pshenichny compared solubility of lanthanide oxides in fluorozirconate melts and found that the solubilities decrease in the increasing order of Ln^{3+} ion radius, i.e. $S_{\text{La}_2\text{O}_3} > S_{\text{Sm}_2\text{O}_3} > S_{\text{Ho}_2\text{O}_3}$, and in the increasing order of alkali metal cation radius in the melts, i.e. $S_{\text{LiF}} > S_{\text{NaF}} > S_{\text{KF}}$ ¹² (see Figure 3). This is consistent with the results from Ambrová ¹⁸. The acidic power of a cation Z was calculated and used to interpret the dissolution behaviour of oxides in the melts ¹². The acidic power of binary systems decreases sequentially as the cationic radius of alkali metal increases. The decrease in solubility of lanthanide oxides can then be associated with the decrease in polarizing power of the cation.

Alkali earth metal fluoride (AF_2) content

The addition of AF_2 in the melts can further lower their melting points together with limiting the evaporation of LiF and lowering the melt viscosity ².

Wu investigated the melt composition before and after dissolution tests and confirmed the positive impact of BaF_2 on preventing evaporation of LiF due to the formation of complexes ⁸.

Figure 4 shows the influence of AF_2 addition on the REO solubility in $\text{LiF-MF}_2\text{-NdF}_3$ melts (M = Mg, Ba). In some cases it has a positive effect while sometimes negative, but the variations are moderate. This suggests that the REO solubility should stay low and stable with AF_2 addition. It could be meaningful in some cases. For example, Nd-Mg alloy prepared by co-electrowinning from an $\text{LiF-MgF}_2\text{-NdF}_3$ melt containing dissolved Nd_2O_3 should be possible as the low solubility of Nd_2O_3 is not reduced by the MgF_2 addition.

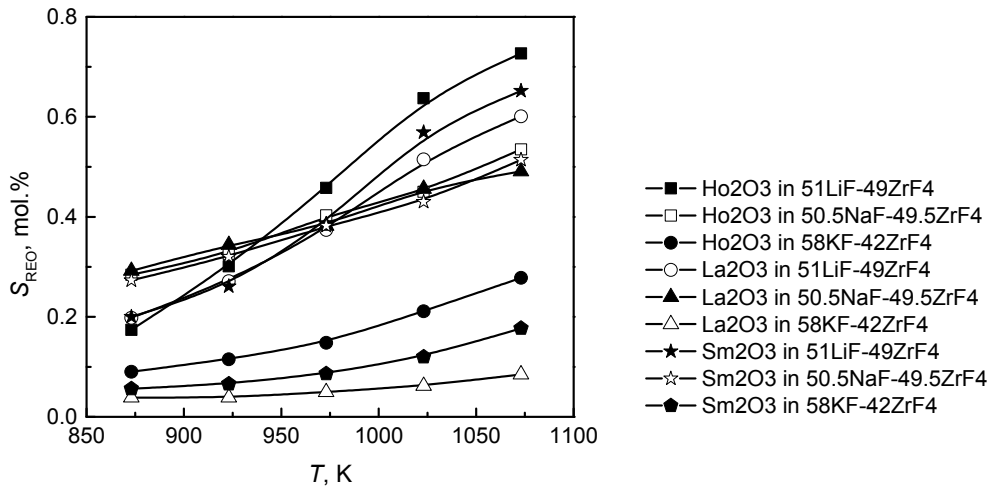


Figure 3 Solubility of lanthanide oxides in fluorozirconate melts (reproduced with data from reference 12)

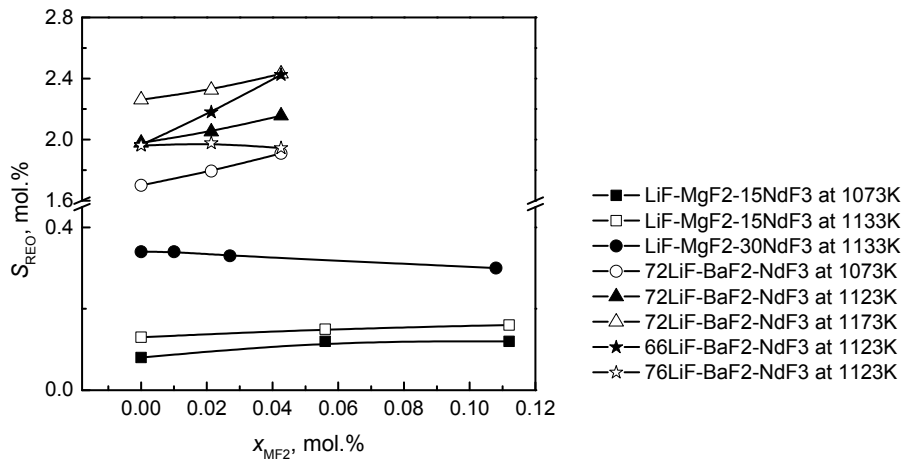


Figure 4 Solubility of Nd_2O_3 in $LiF-MF_2-NdF_3$ melts ($M = Mg, Ba$) (reproduced with data from reference 8 and 10)

Conclusions and future work

This paper comprehensively summarises, reconstructs and analyses the available data from previous publications on the REO solubility in molten fluorides. The REO solubility increases with temperature and RF_3 content. There is a simple linear relationship between the natural logarithm of the solubility and the reciprocal of the absolute temperature. The alkali metal fluoride addition, mostly LiF, can lower the melting points of binary systems and improve their electrical conductivity. The alkali earth metal fluoride, usually as a third additive, can further lower the melting points and limiting the evaporation of LiF.

As a key factor for optimized electrolysis, study on the REO solubility can help the electrolyte selection and feed rate control. A more detailed analysis of the solubility data is needed to

find out a method for estimation of the solubility on the basis of thermodynamic calculations, which would assist selection of electrolyte, aiming for a higher REO solubility without compromising other electrolyte properties (e.g. viscosity, electrical conductivity). More work should be done on the structure of the REO-fluoride system to reveal the mechanism of REO dissolution. Studies on dissolution kinetics will enable a better feed rate control to lead to a smoother cell operation.

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