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Comparative study of the mutual separation characteristics for binary mixed oxides Er_2O_3 - Ln_2O_3 (Ln = Sc, Y, La, Nd, Sm, Gd and Ho) mediated by vapor complexes KLnCl₄

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Abstract

Mutual separation characteristics for a series of rare earth elements Sc, Y, La, Nd, Sm, Gd, Ho and Er from their binary oxide mixtures $Er_2O_3-Sc_2O_3$, $Er_2O_3-H_2O_3$, $Er_2O_3-La_2O_3$, $Er_2O_3-Nd_2O_3$, $Er_2O_3-Sm_2O_3$, $Er_2O_3-Gd_2O_3$ and $Er_2O_3-Ho_2O_3$ has been investigated using a stepwise chlorination-chemical vapor transport (SC-CVT) reaction mediated by vapor complexes KLnCl₄. The total transported yield of the chlorides produced from the oxide mixtures was in the order of $ErCl_3 > ScCl_3$, $ErCl_3 > YCl_3$, $ErCl_3 > LaCl_3$, $ErCl_3 > NdCl_3$, $ErCl_3 > SmCl_3$, $ErCl_3 > GdCl_3$ and $HoCl_3 > ErCl_3$, and the total separation factors are 13.0 for Er:Sc, 1.49 for Er:Y, 1.48 for Er:La, 1.15 for Er:Nd, 2.33 for Er:Sm, 2.72 for Er:Gd and 1.10 for Ho:Er. The largest separation factors 1213.8 for Er:Sc, 6.37 for Er:Y, 189.3 for Er:La, 100.6 for Er:Nd, 105.7 for Er:Sm, 27.8 for Er:Gd and 1.14 for Er:Ho in the lower temperature region, while 102.7 for La:Er, only 14.3 for Nd:Er, 16.7 for Sm:Er, 4.0 for Gd:Er and 2.04 for Ho:Er in the higher temperature region were observed, respectively. The results showed the obvious divergence effect of Gd both in the largest separation factors, the total separation factors and total transport efficiency. Furthermore, the results were discussed on the difference of ionic radius of Sc and Y on the one side and the lanthanoid elements of La, Nd, Sm, Gd, Ho and Er on the other hand, and verified that the ionic radius is one of the decisive factors only for lanthanide elements, not for Sc and Y.

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1. Introduction

Mutual separation characteristics of rare earth elements by a dry process so called chemical vapor transport reaction [1–22] have been investigated intensively from several aspects, such as different vapor complexes KLnCl₄ [2,3,10,13,14,20–22] or LnAl_nCl_{3n+3} [1,4–19], different raw materials like as rare earth chloride mixtures, oxide mixtures, concentrates of ore and the scraps containing of rare earth elements. Moreover, the temperature gradients [4,22] and reaction steps for separation has been investigated too, that is

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the conventional chemical vapor transport (CVT) reaction [1–10,12–14] or stepwise selective chlorination-chemical vapor transport (SC-CVT) reaction [11,15–22]. More efficient separation has been observed for oxide mixtures than for chloride mixtures [10,12–14] and using SC-CVT than using CVT reaction [11,15,17,18], and a further improved separation efficiency and total transport yields realized mediated by KCl or KCl–AlCl₃ as complex former instead of only by AlCl₃ as complex former. Furthermore, the characteristics of CVT or SC-CVT have been discussed from the nature of the rare earth elements such as the ionic structure, ionic radius and the electronic configuration by investigating the mixed oxides which the rare earth elements located in different period of the periodic table [13,14,18,20–22].

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The CVT or SC-CVT mutual separation for the lanthanide elements showed that the ionic radius difference of two elements is one of the decisive factors for the separation efficiency [1-12,15-17,19,21,22], and the separation for Sc and Y from Sc₂O₃-La₂O₃ [13], Y₂O₃-La₂O₃ [13,18,20], Y₂O₃-Nd₂O₃ [18,20], Y₂O₃-Sm₂O₃ [18,20], Y₂O₃-Dy₂O₃ [14,22], Y₂O₃-Ho₂O₃ [14,21], Y₂O₃-Er₂O₃ [14,22] and Ho₂O₃-Sc₂O₃ [21] showed that the ionic structure and the electronic configuration are the key factors in the CVT reaction.

Recently, Wang's group has determined the thermodynamic properties of the gaseous species $LnAl_nCl_{3n+3}$ for all of rare earth elements including Sc and Y, and found that LnAl₃Cl₁₂ is the predominant gaseous complex species for the lanthanide series from La to Lu [24-26] while LnAl₂Cl₉ for Sc and Y [23] in the temperature range from 500 to 900 K. On the other hand, Adachi and co-workers [13,14] have reported the CVT characteristics of the binary oxide mixtures $Sc_2O_3 - Y_2O_3$ [13], $Sc_2O_3 - La_2O_3$ [13] and Y_2O_3 -Ln₂O₃ (Ln = La [13], Dy [14], Ho [14] and Er [14]) mediated by gaseous complexes $LnAl_nCl_{3n+3}$ and KLnCl₄. The experiment results [13,14] indicated that ScCl₃ could be easily separated from YCl₃ and LaCl₃ while the unexpected results that the lowest CVT efficiency and the lowest gaseous complexes stability for YCl3 compared with $LnCl_3$ (Ln = Dy, Ho and Er) were observed. Very recently, we [18,20-22] reported the mutual separation characteristics for Sc, Y, Ho and lanthanoid rare earth elements, such as La, Nd, Sm, Dy and Er from their binary oxide mixtures $Sc_2O_3-Y_2O_3$ [18,20], $Y_2O_3-Ln_2O_3$ (Ln = La [18,20], Nd [18,20], Sm [18,20], Dy [22], Ho [21,22] and Er [22]), $Sc_2O_3-Ho_2O_3$ [21] and $Ho_2O_3-Ln_2O_3$ [21] (Ln = Y, La, Nd and Sm) using SC-CVT reaction mediated by $LnAl_nCl_{3n+3}$ [18] and $KLnCl_4$ [20–22]. The results mainly show the largest total transport yields of YCl₃ compared with that of Sc, La, Nd and Sm mediated by $LnAl_nCl_{3n+3}$, that is $YCl_3 > NdCl_3 > SmCl_3 > LaCl_3 > ScCl_3$ [18] while $NdCl_3 > SmCl_3 > LaCl_3 > YCl_3 > ScCl_3$ mediated by KLnCl₄ [20], and that of LaCl₃ > HoCl₃ > NdCl₃ > SmCl₃ > $YCl_3 > ScCl_3$ [21] and $HoCl_3 > ErCl_3 > DyCl_3 > YCl_3$ [22] mediated by KLnCl₄. Moreover, Sc and La are easily separated from Y and Ho compared with the other elements. Generally, the chlorination ability of Er₂O₃ is as low as that of Ho_2O_3 and Y_2O_3 under normal chlorination conditions, since the ionic radius of erbium is very similar to that of holmium and yttrium. So, the chemical vapor transport characteristics of Er₂O₃-Ln₂O₃ should be close to that of Y₂O₃-Ln₂O₃ [18,20] and Ho₂O₃-Ln₂O₃ [21] mediated by vapor complexes $LnAl_nCl_{3n+4}$ or $KLnCl_4$. Thus, in this study, together with those shown in [22] for Er₂O₃-Y₂O₃ and Er₂O₃-Ho₂O₃, we tried to systematic investigate the mutual separation characteristics for Er, Sc, Y, La, Nd, Sm, Gd and Ho from their binary oxide mixtures Er₂O₃-Sc₂O₃, Er₂O₃-Y₂O₃, Er₂O₃-La₂O₃, Er₂O₃-Nd₂O₃, Er₂O₃-Sm₂O₃, Er₂O₃-Gd₂O₃ and Er₂O₃-Ho₂O₃ using SC-CVT reaction mediated by KLnCl₄.

2. Experimental details

The chemicals used in this study were analytic purity for KCl, active carbon powder and $\geq 99.9\%$ purity for all rare earth oxides. A raw mixture was formed by mixing active carbon and KCl with a binary oxide mixture of rare earth elements Ln and Ln' at an atomic ratio of C:Ln:Ln':K = 6:1:1:1, which contains 3.0–5.0 mmol of each rare earth element, Ln and Ln'.

The SC-CVT reaction was carried out in a cylindrical alumina reactor tube, 25 mm inner diameter and 1000 mm length, with a given temperature gradient as described in previous paper [10–12,15–22]. Let T denote the highest temperature in the tube reactor, where the raw materials were placed. The raw material was chlorinated by dry Cl₂ gas with a flow rate of 20 cm³ min⁻¹ at T = 800 K for 2 h. The Cl₂ gas was replaced by a dry Ar-Cl₂ mixed gas with the flow rates of 30 and 10 cm³ min⁻¹, respectively, within the temperature range of T = 800 - 1300 K. Then, the rare earth chlorides reacted with KCl to form the vapor complexes KLnCl₄, which were transported chemically along the temperature gradient in the tube reactor at T = 1300 K for 6 h with the Ar–Cl₂ carrier gas. At the end of each run, the amounts of the rare earth chloride produced were determined from the peak intensity of the characteristic bands: 337.271 nm for Er^{3+} , 337.215 nm for $Sc^{3+},\,377.433\,nm$ for $Y^{3+},\,333.749\,nm$ for $La^{3+},\,401.225\,nm$ for Nd^{3+} , 359.260 nm for Sm^{3+} , 342.247 nm for Gd^{3+} and 339.898 nm for Ho³⁺, on an inductively coupled plasma atomic emission spectrometry (Perkin-Elmer, Optima 2000).

3. Results and discussion

3.1. Mutual separation for Er_2O_3 - Ln_2O_3 (Ln = Sc, Y, La, Nd, Sm, Gd and Ho)

Fig. 1(A–G) show the SC-CVT reaction results of the binary oxide mixtures $Er_2O_3-Sc_2O_3$, $Er_2O_3-La_2O_3$, $Er_2O_3-Nd_2O_3$, $Er_2O_3-Sm_2O_3$, $Er_2O_3-Gd_2O_3$ determined in this study, together with those of $Er_2O_3-Y_2O_3$ [22] and $Er_2O_3-Ho_2O_3$ [22], in the form of deposition profiles for the rare earth chlorides transported versus fraction numbers (FN) of the receptors, taking KCl as complex former and Argon gas as carried gas in the given temperature gradient for 6 h.

It can be seen that there are few ScCl₃ deposited in the receptor from FN = 1–7, and only a very small amounts of ScCl₃ concentrates in the lower temperature region from 1050 to 900 K (FN = 8–12) indicated that the vapor complexes KScCl₄ is stable in the higher temperature range and decomposed only in the lower temperatures region, while ErCl₃ mainly distributes in the middle temperature range from 1120 to 980 K (FN = 5–10). For Er–Y system [22], the main distribution temperature of both ErCl₃ and YCl₃ concentrated in 1000–750 K (FN = 9–14). For lanthanoid elements Er–Ln (Ln = La, Nd, Sm, Gd and Ho [22]), the distribution of chlorides was in accordance with the ionic





Fig. 1. Temperature gradients and distribution of ErCl₃, ScCl₃, YCl₃, LaCl₃, NdCl₃, SmCl₃, GdCl₃ and HoCl₃, deposit in SC-CVT reaction formed from the binary oxide mixtures: (A) $Er_2O_3-Sc_2O_3$, (B) $Er_2O_3-Y_2O_3$, (C) $Er_2O_3-La_2O_3$, (D) $Er_2O_3-Nd_2O_3$, (E) $Er_2O_3-Sm_2O_3$, (F) $Er_2O_3-Gd_2O_3$ and (G) $Er_2O_3-Ho_2O_3$.

radius-stability rule, that is ErCl₃ with smaller lanthanide ion radius concentrates in the lower temperature region while LaCl₃, NdCl₃ and SmCl₃, mainly deposits in the higher temperature region above 1150 K and in the increasing order of SmCl₃ < NdCl₃ < LaCl₃ with the increase of the lanthanide ionic radius size. GdCl₃ and HoCl₃ are all concentrated in the middle temperature region from 1150 to 980 K (FN = 5–10). Moreover, the amounts of chlorides ErCl₃ deposited in the higher temperature region was always smaller than that of LaCl₃, NdCl₃, SmCl₃, GdCl₃ and HoCl₃ and in the lower temperature region, the situation was reversed. All of these are similar to the main deposition region for ScCl₃, YCl₃, HoCl₃, LaCl₃, NdCl₃ and SmCl₃ in previous paper using AlCl₃ [18] and KCl [20,21] as complex former except for ScCl₃ mediated by ScAl_nCl_{3n+3} [18].

1400

1200

800

600

400

2 3 4

5678

<u>У</u> 1000 L

> Table 1 lists the total transported yields of LnCl₃ produced from their oxide mixtures in the SC-CVT reaction. The total transport yields showed that the SC-CVT transport ability is $ErCl_3 > ScCl_3$, $ErCl_3 > YCl_3$, $ErCl_3 > LaCl_3$, $ErCl_3 > NdCl_3$, $ErCl_3 > SmCl_3$, $ErCl_3 > GdCl_3$ while $ErCl_3 < HoCl_3$. From La to Er, the transported yield of LnCl₃ was increasing with the decreasing of the ionic radius of rare earth and the divergence appeared around Sm and Gd, and that of Ho and Er showed abnormal order too. Table 2 lists the total separation factors and the largest values of the separation factor expressed as the atomic ratio for the resulting chlorides. The largest separation factors showed that all the seven binary oxide mixtures achieved better separation effect in some receptor by only one circle of CVT reaction except of Ho₂O₃–Er₂O₃. Particularly, it is easy to make mutual

Table 1 The total transported yields of rare earth chlorides $LnCl_3$ produced from their oxide mixtures Er_2O_3 - Ln_2O_3 (Ln = Sc, Y, La, Nd, Sm, Gd and Ho) through SC-CVT reaction

	Yield (%)							
	Sc	Y	La	Nd	Sm	Gd	Но	Er
Er ₂ O ₃ -Sc ₂ O ₃	1.78							23.12
Er ₂ O ₃ -Y ₂ O ₃		21.33						31.74
Er ₂ O ₃ -La ₂ O ₃			24.85					36.89
Er ₂ O ₃ -Nd ₂ O ₃				31.96				36.75
Er ₂ O ₃ -Sm ₂ O ₃					23.82			55.49
$Er_2O_3-Gd_2O_3$						14.91		40.58
Er ₂ O ₃ -Ho ₂ O ₃							47.72	43.54

separation of Sc_2O_3 from Er_2O_3 by the SC-CVT reaction mediated by vapor complex KLnCl₄.

Fig. 2 gives the total separation factors of Er:Ln, the largest separation factors of Er:Ln or Ln:Er in the lower or higher temperature region, resulted from their binary oxide mixtures versus the ionic radii, here Ln presented La, Nd, Sm, Gd, Ho and Y. The largest separation factors Er:Ln in the lower temperature region is decreasing from 189.3 for Er:La to 100.0 for Er:Nd, and then increased to 105.7 for Er:Sm and sharply decreased to 27.8 for Er:Gd and 1.14 for Er:Ho [22], and the similar phenomena was presented for Ln:Er in the higher temperature region. Moreover, the total separation factors decreased from 1.48 for Er:La to 1.10 for Er:Ho [22], while 2.33 for Er:Sm and 2.72 for Er:Gd which imply that the CVT separation characteristics also showing the Gd divergence for the lanthanoid elements. In addition, the largest separation factor 6.37 for Er:Y [22] is much larger than that 1.14 for Er:Ho which showed that the separation characteristic for Y by CVT method does not depend on the ionic radius of Y³⁺.

Table 2

The largest	separation	factors,	total	separation	factors	between	rare	earth
elements Er	, Sc, Y, La,	Nd, Sm,	Gd a	nd Ho from	their bi	nary oxid	e mix	tures
using a SC-	CVT reacti	on						

	SF ^a	FN ^b	TSF ^c
Er ₂ O ₃ –Sc ₂ O ₃	1213.8 (Er:Sc)	9	13.0 (Er:Sc)
$Er_2O_3-Y_2O_3$	6.37 (Er:Y) 1.25 (Y:Er)	12 14	1.49 (Er:Y)
Er ₂ O ₃ -La ₂ O ₃	189.3 (Er:La) 102.7 (La:Er)	9 1	1.48 (Er:La)
$Er_2O_3-Nd_2O_3$	100.0 (Er:Nd) 14.3 (Nd:Er)	9 4	1.15 (Er:Nd)
Er_2O_3 – Sm_2O_3	105.7 (Er:Sm) 16.7 (Sm:Er)	10 1	2.33 (Er:Sm)
$Er_2O_3-Gd_2O_3$	27.8 (Er:Gd) 4.02 (Gd:Er)	10 3	2.72 (Er:Gd)
Er ₂ O ₃ -Ho ₂ O ₃	2.04 (Ho:Er) 1.14 (Er:Ho)	8 12	1.10 (Ho:Er)

^a SF, separation factor.

^b FN, fraction number.

^c TSF, total separation factor.

3.2. The mechanism of SC-CVT reaction

The SC-CVT reaction mechanism might mainly be a combination of selective carbon thermic reduction-chlorination sub-reaction of the oxides at T = 800 K:

$$\frac{1}{2}Ln_2O_3(s) + \frac{3}{2}Cl_2(g) + \frac{3}{2}C(s) = LnCl_3(s) + \frac{3}{2}CO(g)$$

(Ln = Er, Sc, Y, La, Nd, Sm, Gd and Ho) (1)

exchange sub-reactions between the remaining oxides and the produced chlorides within the temperature range of T = 800-1300 K:

$$\frac{1}{2}Ln_2O_3(s) + Ln'Cl_3(l \text{ or } s) = LnCl_3(l \text{ or } s) + \frac{1}{2}Ln'_2O_3(s)$$
$$(Ln \neq Ln' = Er, Sc, Y, La, Nd, Sm, Gd and Ho)$$
(2)

selective complex formation sub-reactions of the produced chlorides at T = 1300 K:

$$LnCl_{3}(l) + KCl(l) = KLnCl_{4}(g)$$

$$(Ln = Er, Sc, Y, La, Nd, Sm, Gd and Ho)$$
(3)



Fig. 2. Separation factors of the Er–Ln (Ln=Y, La, Nd, Sm, Gd and Ho) resulted from their binary oxide mixtures vs. the ionic radii. (\bigcirc) Ln:Er; (\bigcirc) Er:Ln; (\times) TSF of Er:Ln.

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and selective CVT sub-reactions of the vapor complexes KLnCl₄ along the temperature gradient:

$$KLnCl_4(g) = LnCl_3(l \text{ or } s) + KCl(s \text{ or } l)$$

(Ln = Er, Sc, Y, La, Nd, Sm, Gd and Ho) (4)

The total transported amount of $LnCl_3$ would mainly be determined by the gas–solid reaction (1), solid–solid or liquid–solid reaction (2) and liquid–liquid reaction (3), while the distribution characteristics of $LnCl_3$ in the reactor tube would mainly be determined by the vapor complexes selective CVT sub-reactions (4) along the temperature gradients.

3.3. Discussion

The complexation ability of $KLnCl_4$ (Ln = Er, Sc, Y, La, Nd, Sm, Gd and Ho) is determined by the Gibbs free energy changes for the formation $(\Delta_f G^\circ)$ of complexes KLnCl₄. D.S. Mcphail reviewed the data of $\Delta_f G^\circ$ at 1000 K for the reaction $LnCl_3(l) + KCl(l) = KLnCl_4(g)$ are $-106.8 \text{ kJ mol}^{-1}$ for KErCl_4 , $-103.0 \text{ kJ mol}^{-1}$ for KScCl_4 [27], $-121.0 \text{ kJ mol}^{-1}$ for KYCl₄ [27], $-129.0 \text{ kJ} \text{ mol}^{-1}$ for KLaCl₄ [27] and $-115.0 \text{ kJ mol}^{-1}$ for KNdCl₄ [27], $-126.0 \text{ kJ mol}^{-1}$ for $KGdCl_4$ [27], -117.0 kJ mol⁻¹ for KHoCl₄ [27] and there no thermodynamic data for KSmCl₄ until now. According to the $\Delta_{\rm f} G^{\circ}$ data, the ratio of equilibrium vapor pressure of the complexes KLnCl₄ at 1300 K can be estimated: 1.42 for Er:Sc, 0.268 for Er:Y, 0.128 for Er:La, 0.468 for Er:Nd, 0.169 for Er:Gd and 0.389 for Er:Ho, indicating that the formation ability of vapor complexes is in the order of Er > Sc, Er < Y, Er < La, Er < Nd, Er < Gd and Er < Ho, which is different from the SC-CVT results of Er > Y, Er > La, Er > Nd and Er > Gdin this study.

On the other hand, according to thermochemical data [28], the ratios of equilibrium constants of the carbonthermic reduction-chlorination sub-reaction (1) for Er_2O_3 and Ln_2O_3 , $\{K_1(\text{Er})/K_1(\text{Ln})\}$, which are equivalent to the equilibrium constant of the exchange sub-reaction (2), were calculated to be, 2.93×10^4 for Er/Sc, 7.0×10^{-2} for Er/Y, 4.48×10^{-11} for Er/La, 7.46×10^{-9} for Er/Nd, 3.42×10^{-7} for Er/Sm, 1.00×10^{-8} for Er/Gd and 3.64×10^{-4} for Er/Ho at 800 K and 90.91 for Er/Sc, 4.5×10^{-2} for Er/Y, 3.62×10^{-7} for Er/La, 1.33×10^{-7} for Er/Nd, 4.72×10^{-5} for Er/Sm, 1.43×10^{-7} for Er/Gd and 9.17×10^{-4} for Er/Ho at 1300 K. That is, the amount of chlorides formed is expected as $ErCl_3 > ScCl_3, ErCl_3 < YCl_3, ErCl_3 < LaCl_3, ErCl_3 < NdCl_3,$ $ErCl_3 < SmCl_3$, $ErCl_3 < GdCl_3$ and $ErCl_3 < HoCl_3$, some of which are different from the SC-CVT results: ErCl₃ > YCl₃, ErCl₃ > LaCl₃, ErCl₃ > NdCl₃, ErCl₃ > SmCl₃ and $ErCl_3 > GdCl_3$. This may be easy to understand from the fact that KErCl₄ is more volatile and thus more stable than $KLnCl_4$ (Ln = Y, La, Nd and Gd) deduced from the volatility of the simple $LnCl_3$ (Ln = Er, Y, La, Nd and Gd) [29].

In addition, our preliminary experiment also showed that the selective chlorination of the raw materials with dry Cl_2 gas at T = 800 K for 2 h might result in an yield of 51.8% for ErCl₃ while Sc₂O₃ is only 9.7%, and the chlorides yields ratio is 5.35 for Er:Sc, 1.23 for Er:Y [22], 2.24 for Er:La, 1.04 for Er:Nd, 1.05 for Er:Sm, 1.33 for Er:Gd and 1.05 for Ho:Er [22]. This agrees with the results of total transport yields of ErCl₃ > ScCl₃, ErCl₃ > YCl₃, ErCl₃ > LaCl₃, ErCl₃ > NdCl₃, ErCl₃ > SmCl₃, ErCl₃ > GdCl₃ and HoCl₃ > ErCl₃ in this study. As mentioned above, the SC-CVT results is a combination of selective chlorination in the lower temperature and the complexation and CVT reaction in the higher temperature.

The largest separation factor of 1213.8 for Er:Sc in this study is closed to that of 1480 for Ho:Sc [21] and 1100 for Y:Sc [20] by SC-CVT with KCl as complex former, and much higher than those for the SC-CVT results of 29.9 for Y:Sc [18] and CVT results 16.9 for Y:Sc [13] mediated by $LnAl_nCl_{3n+3}$, and 22.26 for Y:Sc by conventional CVT [13] with KCl as complex former. This might be explained as follows: vapor complexes $LnAl_nCl_{3n+3}$ for Sc has higher stability than that for Y [23], while KLnCl₄ for Y, Ho and Er has higher stability than that of Sc [27]. Thus, the vapor pressure ratio of $LnAl_nCl_{3n+3}$ is 3.13 for Sc:Y, and that of KLnCl₄ is 5.29 for Y:Sc, 3.65 for Ho:Sc and 1.42 for Er:Sc. On the other hand, however, the selective chlorination ability of Sc_2O_3 is much lower than that of Y₂O₃, Ho₂O₃ and Er₂O₃, so the separation efficiency for Y:Sc mediated by LnAl_nCl_{3n+3} using a SC-CVT reaction was weaken.

Moreover, although the ionic radius of Er^{3+} is similar to that for Ho³⁺ and Y³⁺, Y, Ho and Er located at different period of the periodic table, suggesting result the difference of Y³⁺ in ionic structure and electronic configuration to the lanthanide elements, i.e. the stable structure of [Kr] for Y³⁺ while [Xe] 4f¹⁰ for Ho³⁺ and [Xe] 4f¹¹ for Er³⁺ which can result in the separation efficiency of Er:Sc and Ho:Sc higher than that of Y:Sc mediated by KLnCl₄.

In the situation of Er-Y [22], the largest separation factors 6.37 for Er:Y in this study is lower than that of 15.3 for Ho:Y under the same reaction condition [21], this maybe denoted by the volatility of complex KHoCl₄ is higher than that of KErCl₄ which showed in this study and [14]. But the value is higher than that of 1.54 for Er:Y, 1.11 for Ho:Y mediated by KLnCl₄ in the CVT reaction [14], this maybe explained as the selective chlorination in the lower temperature 800 K in this study while 1300 K in [14].

For Er–Ln (Ln = La, Nd, Sm, Gd and Ho [22]) systems, the largest separation factors Er:Ln in the lower temperature region or Ln:Er in the higher temperature region listed in Table 2 are corresponding to the rule that the larger the difference between the two ionic radius, the greater the separation factor of two lanthanide elements from CVT reaction. Here the separation factors for Er–Nd and Er–Sm do not agree with the rule mentioned above. This abnormal phenomena for Nd and Sm observed in the Y–Nd [20], Y–Sm [20], Ho–Nd [21] and Ho–Sm [21] systems too. This cannot be explained from the point of view of thermodynamics since there are no thermodynamic data for KSmCl₄ until now. In additional, the temperature region where the largest

separation efficiency occurred for Er-Ln (Ln = Sc, La, Nd and Sm) was very near to that of Ho-Ln [21] and Y-Ln (Ln = Sc, La, Nd and Sm) [20] mediated by KLnCl₄. Furthermore, considering the difference of ionic radius of two rare earth elements of 14.2 pm for Δ (La–Er), 9.3 pm for Δ (Nd–Er), 6.8 pm for Δ (Sm–Er), 4.8 pm for Δ (Gd–Er) and only 1.0 pm for Δ (Y–Er) and 1.1 pm for (Ho–Er), the experiment results are very interest, for the separation factors 102.7 for La:Er or 189.3 for Er:La are much higher than that of 14.3 for Nd:Er or 100.0 for Er:Nd, this may be caused by the electron orbital of La³⁺ only contain 4f hybridization electrons [30] not the true 4f electrons. While the separation factor for Y:Er or Er:Y does not depend on the difference of ionic radius of Y and Er, this is similar to that for Y and Ho [21]. Thus, the results clearly proved that the ionic radius is one of the decisive factors of stability of the gaseous complexes only for lanthanide elements, not including Sc and Y.

4. Conclusions

A comparative study has been carried out for SC-CVT characteristics of binary oxide mixtures of Er, Sc, Y, La, Nd, Sm, Gd and Ho from Er₂O₃–Sc₂O₃, Er₂O₃–Y₂O₃, Er₂O₃-La₂O₃, Er₂O₃-Nd₂O₃, Er₂O₃-Sm₂O₃, Er₂O₃-Gd₂ O_3 and Er_2O_3 -Ho₂O₃, via vapor complexes KLnCl₄. The results were discussed on the difference of ionic structure of Sc and Y on the one side and 4f lanthanide elements of La, Nd, Sm, Gd, Ho and Er on the other hand, which showed that the ionic radius is one of the decisive factors of stability of the gaseous complexes only for lanthanide elements, not for Sc and Y. Moreover, the results showed the obvious divergence of Gd both in the largest separation factors, the total separation factors and total transport efficiency. Furthermore, the SC-CVT characteristics mediated by vapor complexes KLnCl₄ of binary oxides Er₂O₃-Ln₂O₃ were similar to that of Ho₂O₃-Ln₂O₃ and Y₂O₃-Ln₂O₃ mediated by KLnCl₄ for the ionic radius of Er^{3+} , Ho^{3+} and Y^{3+} are very near.

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