

Mutual separation characteristics for binary oxides $\text{Y}_2\text{O}_3\text{-Ln}_2\text{O}_3$ ($\text{Ln} = \text{Sc, La, Nd, Sm}$) using stepwise selective chlorination-chemical vapor transport reaction mediated by vapor complexes KLnCl_4 ^①

SUN Yan-hui(孙艳辉)¹, CHEN Zhen-fei(陈振飞)², WANG Zhi-chang(王之昌)³

(1. Department of Chemistry, South China Normal University, Guangzhou 510631, China;

2. Department of Metallurgy, Hebei Institute of Technology, Tangshan 063009, China;

3. Department of Chemistry, Northeastern University, Shenyang 110006, China)

Abstract: Mutual separation characteristics for binary oxide mixtures $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-La}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Sm}_2\text{O}_3$ using a stepwise selective chlorination-chemical vapor transport(SC-CVT) reaction mediated by vapor complexes KLnCl_4 were investigated. The total transported yields of the chlorides produced from the oxide mixtures are in the order of $\text{NdCl}_3 > \text{SmCl}_3 > \text{LaCl}_3 > \text{YCl}_3 > \text{ScCl}_3$, the main deposition temperature of the chlorides is in the order of $\text{ScCl}_3 < \text{YCl}_3 < \text{SmCl}_3 < \text{NdCl}_3 < \text{LaCl}_3$, and the largest separation factor values are 1.100 for Y: Sc, 14.88 for Y: La, 9.86 for Y: Nd and 16.45 for Y: Sm in the temperature range from 1 000 K to 1 120 K, while 157.7 for La: Y, 51.6 for Nd: Y and 12.4 for Sm: Y in the temperature range from 1 200 K to 1 300 K, respectively. The results were discussed on the difference of KScCl_4 , KYCl_4 and KLnCl_4 and the selective chlorination of binary oxides at 800 K. Furthermore, the separation characteristics of vapor rare earth complex KLnCl_4 were studied compared with those of $\text{LnAl}_n\text{Cl}_{3n+3}$.

Key words: rare earth oxides; separation; chemical vapor transport reaction; KLnCl_4

CLC number: TQ 133.1; O 614.33

Document code: A

1 INTRODUCTION

As we all know, although the vapor rare earth complexes possess the same important role as the solid and liquid state complexes in rare earth chemistry, the study of vapor rare earth complexes is relatively slow. Recently, Boghosian et al.^[1] and JIANG et al.^[2] reviewed the study panorama of the vapor rare earth complexes. The rare earth vapor complexes $\text{LnAl}_n\text{Cl}_{3n+3}$ and ALnCl_4 , where A represents alkali-line metal and Ln represents rare earth elements, have been used as intermediate materials for the preparation of anhydrous rare earth chlorides in high purity^[3-5], for mutual separation of rare earth elements^[6-14], and for recovery of rare earth metals from rare earth crude ore^[15] or scrap of rare earth intermetallic material^[16] by using chemical vapor transport(CVT) or stepwise selective chlorination-CVT(SC-CVT) reactions. The CVT separation is found to be more efficient when being mediated by KLnCl_4 and taking KCl as complex former than that when being mediated by $\text{LnAl}_n\text{Cl}_{3n+3}$ and taking AlCl_3 as complex former. And it is more efficient through SC-CVT than conventional CVT reaction due to the thermodynamic and kinetic reasons.

WANG et al.^[3-5] determined the thermodynamic properties of the gaseous species $\text{LnAl}_n\text{Cl}_{3n+3}$ for all of rare earth elements including Sc and Y, and found that $\text{LnAl}_3\text{Cl}_{12}$ is the predominant gaseous complex species for the series lanthanide from La to Lu; while LnAl_2Cl_9 for Sc and Y in the temperature range from 500 K to 900 K. Recently, Adachi et al.^[6] reported the CVT characteristics of the binary oxide mixtures $\text{Sc}_2\text{O}_3\text{-Y}_2\text{O}_3$, $\text{Sc}_2\text{O}_3\text{-La}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-La}_2\text{O}_3$ mediated by gaseous $\text{LnAl}_n\text{Cl}_{3n+3}$ and KLnCl_4 . The experiment results indicated that ScCl_3 could be easily separated from YCl_3 and LaCl_3 by the dry CVT process and provided an indirect support for the viewpoint that La^{3+} in fact contains 4f composition due to its electron hybridization assumed by Gschneidner^[17]. Very recently, we reported the mutual separation characteristics for Sc, Y and the rare earth elements such as La, Nd and Sm which usually coexisted in monazite ores from their binary oxide mixtures $\text{Y}_2\text{O}_3\text{-Ln}_2\text{O}_3$ ($\text{Ln} = \text{Sc, La, Nd and Sm}$) using SC-CVT reaction mediated by $\text{LnAl}_n\text{Cl}_{3n+3}$ ^[14]. The results mainly showed the SC-CVT characteristic difference between the rare earth elements Sc and Y and the lanthanide elements La, Nd and Sm. This was con-

① **Foundation item:** Project(501272) supported by the Natural Science Foundation of Hebei Province, China

Received date: 2003 - 06 - 16; **Accepted date:** 2003 - 10 - 24

Correspondence: SUN Yan-hui, PhD; E-mail: sunyanhui0102@163.com

sistent with Adachi's CVT separation results for the binary oxide mixtures $\text{Ln}_2\text{O}_3\text{-Ln}'_2\text{O}_3$ ($\text{Ln} \neq \text{Ln}' = \text{Sc, Y, La}$) via the vapor complexes $\text{LnAl}_n\text{Cl}_{3n+3}$ ^[12]. Moreover, the results showed that the SC-CVT separation efficient is higher than that the CVT reaction efficient. But there was no evidence to prove that the SC-CVT characteristics of Sc and Y mediated by KScCl_4 and KYCl_4 were different from other lanthanide elements mediated by KLnCl_4 ($\text{Ln} = \text{lanthanides}$) as remarkably as that Sc and Y mediated by $\text{ScAl}_n\text{Cl}_{3n+3}$ and $\text{YAl}_n\text{Cl}_{3n+3}$ from La, Nd and Sm mediated by $\text{LnAl}_n\text{Cl}_{3n+3}$ ^[14].

In this study, we investigate the mutual separation characteristics for Sc, Y, La, Nd and Sm from their binary oxide mixtures $\text{Sc}_2\text{O}_3\text{-Y}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-La}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Sm}_2\text{O}_3$ using SC-CVT reaction mediated by KLnCl_4 .

2 EXPERIMENTAL

The chemicals used in this study were analytically pure for KCl and active carbon, and had a purity equal to or more than 99.9% 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' with molar ratio of $x(\text{C}):x(\text{Ln}):x(\text{Ln}'):x(\text{K}) = 6:1:1:1$, which contains about 5.0 mmol rare earth elements for Ln and Ln' , respectively.

The SC-CVT reaction was carried out in a cylindrical alumina reactor tube, with 25 mm in inner diameter, 32 mm in outer diameter and 1 000 mm in length. A given temperature gradients are shown in Fig. 1. Fifteen pieces of alumina receptor tube with 17 mm in inner diameter, 24 mm in outer diameter and 50 mm in length were placed besides the graphite react boat where the raw materials

were filled. Let T_{\max} denoted the highest temperature in the tube reactor, where the raw material was placed. The raw material was chlorinated by dry Cl_2 with a flow rate of $20 \text{ cm}^3/\text{min}$ at $T_{\max} = 800 \text{ K}$ for 2 h. The Cl_2 was replaced by a dry $\text{Ar} + \text{Cl}_2$ mixed gas with the flow rates of $30 \text{ cm}^3/\text{min}$ and $10 \text{ cm}^3/\text{min}$, respectively, within the temperature range of $T_{\max} = 800 - 1300 \text{ K}$. Then, the rare earth chlorides reacted with KCl to form the vapor complexes KLnCl_4 and the vapor complexes chemically transported along the temperature gradient in the tube reactor at $T_{\max} = 1300 \text{ K}$ for 6 h, using a dry $\text{Ar} + \text{Cl}_2$ mixed gas with the flow rates of $30 \text{ cm}^3/\text{min}$ and $10 \text{ cm}^3/\text{min}$ as the carried 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 Sc^{3+} , 377.433 nm for Y^{3+} , 333.749 nm for La^{3+} , 401.225 nm for Nd^{3+} and 359.260 nm for Sm^{3+} on an inductively coupled plasma atomic emission spectrometry (Perkin Elmer, Optima 2000).

3 RESULTS AND DISCUSSION

3.1 SC-CVT characteristics

Fig. 2 shows the SC-CVT reaction results of the binary oxide mixtures $\text{Sc}_2\text{O}_3\text{-Y}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-La}_2\text{O}_3$, $\text{Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Sm}_2\text{O}_3$, in the form of deposition amount for the rare earth chlorides produced vs the receptor tube numbers, taking KCl as complex former and argon gas as carrying gas for 6 h. It can be seen that in Y-Sc system, there is no ScCl_3 deposited in the receptor tube from No. 1 to 12 and only a very small amounts of ScCl_3 concentrate in the temperature range from 900 K to 600 K . YCl_3 mainly distributes in the temperature range from 1160 K to 960 K ; while LaCl_3 , NdCl_3 and SmCl_3 mainly deposit in the temperature range above 1120 K and YCl_3 mainly in

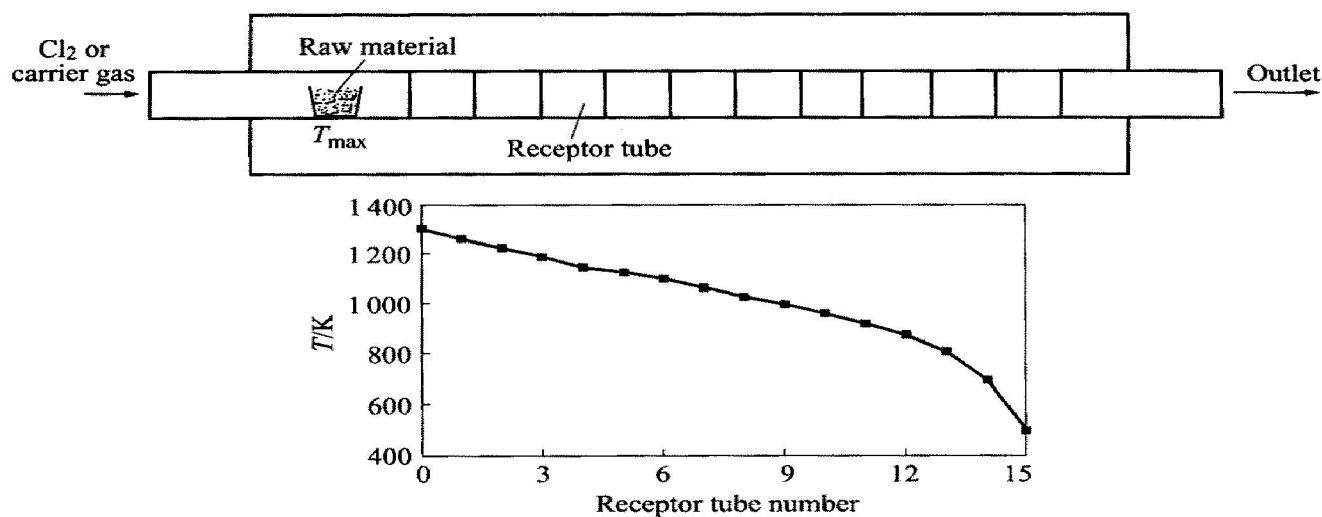


Fig. 1 Schematic representation of reactor and temperature gradients for SC-CVT reaction

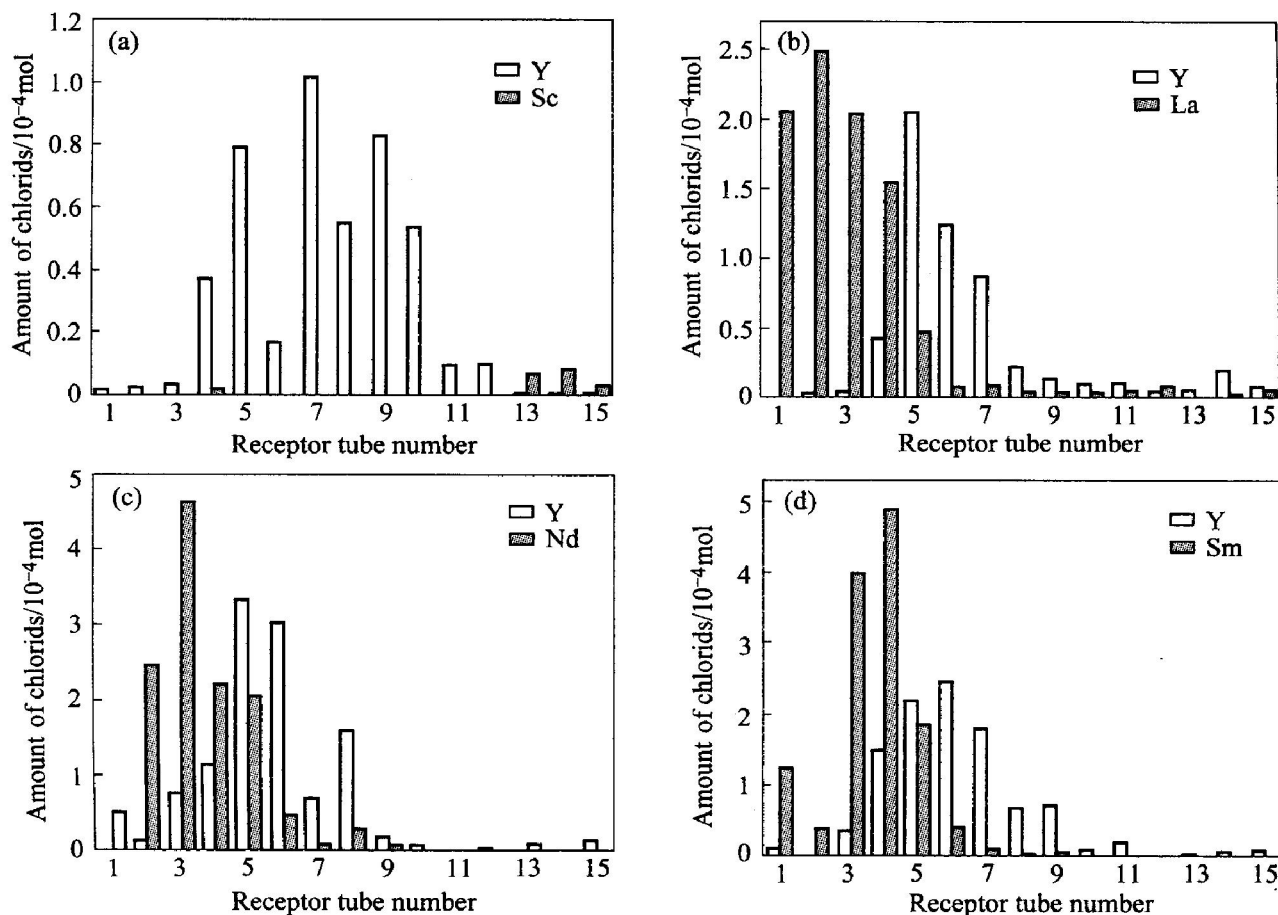


Fig. 2 Distribution of LnCl_3 deposits in SC-CVT reaction formed from their binary oxide mixtures mediated by vapor complexes KLnCl_4
 (a) $-\text{Y}_2\text{O}_3-\text{Sc}_2\text{O}_3$; (b) $-\text{Y}_2\text{O}_3-\text{La}_2\text{O}_3$; (c) $-\text{Y}_2\text{O}_3-\text{Nd}_2\text{O}_3$, (d) $-\text{Y}_2\text{O}_3-\text{Sm}_2\text{O}_3$

the temperature range from 1 160 K to 1 050 K in Y-Ln (Ln = La, Nd and Sm) systems. This is as the same as the main deposition range in previous paper^[14] using AlCl_3 as complex former except for ScCl_3 . And for ScCl_3 , YCl_3 and LaCl_3 , the results was corresponded to the conventional CVT results observed by Adachi^[6] with KCl as complex former. In the situation of Y-La, Y-Nd and Y-Sm system, the amount of chlorides YCl_3 deposited in the higher temperature is always fewer than those of lanthanide chlorides LaCl_3 , NdCl_3 and SmCl_3 , and in the lower temperature range the case is reversed. The results indicate that the stability of the vapor complexes KScCl_4 and KYCl_4 is higher than that of KLnCl_4 (Ln = La, Nd and Sm), where KScCl_4 is stable in the temperature range from 1 300 K to 900 K, KYCl_4 is stable in the temperature range from 1 300 K to 1 160 K, while the early lanthanide complexes are unstable even in the higher temperature 1 300 K, which agrees with that the more the volatile of the chlorides, the more stable the vapor complexes.

3.2 Separation results

The total transported yields of LnCl_3 produced from their oxides, the total separation factors and the

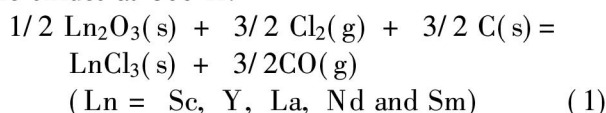
largest values of the separation factor expressed as the molar ratio for the resulting chlorides are listed in Table 1. The largest separation factor values of 1 100 for Y: Sc, 14.88 for Y: La, 9.86 for Y: Nd and 16.45 for Y: Sm in the temperature range from 1 000 K to 1 120 K, and 157.70 for La: Y, 51.60 for Nd: Y and 12.46 for Sm: Y in the temperature range from 1 200 K to 1 300 K were observed, respectively. All of them indicate the potential applicability of the SC-CVT reaction for the rare earth separation. The largest separation factor value of 157.70 for La: Y in this study indicates that the SC-CVT characteristics for Y and La are very different and this provides a new indirect support for Gschneidner's assumption^[17] that the electronic orbital of La^{3+} in fact contains 4f composition due to its electron hybridization, too. The separation factors are much higher than those for the CVT results of 22.26 for Y: Sc, 3.17 for La: Y with KCl as complex former obtained by Adachi^[6], and are higher than those of the SC-CVT results (29.9 for Y: Sc, 10.1 for La: Y in our previous paper)^[14]. In addition, for Nd: Y and Y-Sm, the separation results in this study are much higher than those of 9.09 for Nd: Y and 3.38 for Y: Nd, 2.46 for Y: Sm and 2.38 for Sm: Y in Ref. [14]. All are attributed to the difference in chlorination tempera-

tures, 1 300 K in Ref. [12] and 800 K in this study, and to the thermodynamic characteristics of vapor complexes KLnCl₄ in this study and LnAl_nCl_{3n+3} in Ref. [14] at different temperatures.

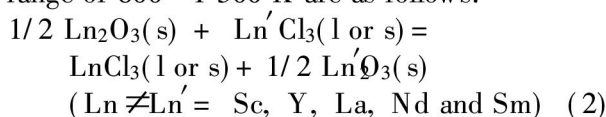
Table 1 Transported yields, largest separation factors and total separation factors of LnCl₃ and Ln'Cl₃ (Ln ≠ Ln' = Sc, Y, La, Nd and Sm) obtained from their binary oxide mixtures in SC-CVT reaction using KCl as complex former

System	Separation factor	Receptor tube number	Transported yield/ %	Total separation factor
Y ₂ O ₃ -Sc ₂ O ₃	1100 (Y: Sc)	8	Y: 11.48 Sc: 0.087	128.80 (Y: Sc)
Y ₂ O ₃ -La ₂ O ₃	14.88 (Y: La)	6	Y: 14.19 La: 22.84	1.62 (La: Y)
Y ₂ O ₃ -Nd ₂ O ₃	9.86 (Y: Nd)	7	Y: 31.12 Nd: 36.01	1.16 (Nd: Y)
Y ₂ O ₃ -Sm ₂ O ₃	16.45 (Y: Sm)	7	Y: 25.22 Sm: 31.92	1.26 (Sm: Y)

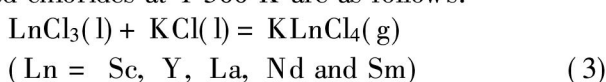
The SC-CVT reaction mechanism for rare earth binary oxide mixtures would be more complicated than that for individual rare earth oxides and the conventional CVT process for rare earth binary oxide mixtures. It might mainly be a combination of selective carbonthermic reduction-chlorination subreaction of the oxides at 800 K:



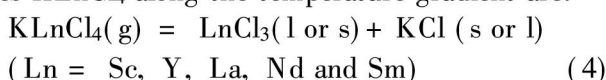
Exchange subreactions between the remained oxides and the produced chlorides within the temperature range of 800–1 300 K are as follows:



Selective complexation subreactions of the produced chlorides at 1 300 K are as follows:



Selective CVT subreactions of the vapor complexes KLnCl₄ along the temperature gradient are:



The total transported amount of LnCl₃ would mainly be determined by the selective carbonthermic reduction-chlorination subreaction of the oxides, exchange subreaction between the remained oxides and the produced chlorides and selective complexation subreaction of rare earth chlorides. While the distribution characteristics of LnCl₃ in the receptor tube would mainly be determined by the selective CVT subreactions along the temperature gradients.

The complexation ability of KLnCl₄ (Ln = Sc, Y, La, Nd and Sm) is determined by the Gibbs free

energy of formation (Δ_fG[⊖]) of complexes KLnCl₄ at different temperatures. Mcphail et al.^[18] and JIANG et al.^[2] reviewed the values of Δ_fG[⊖] for rare earth vapor complexes KLnCl₄ at 1 000 K being – 103 kJ/mol for Sc^[2], – 121 kJ/mol for Y^[18], – 129 kJ/mol for La^[18], – 115 kJ/mol for Nd^[18], and there are no thermodynamic data for Sm until now. So the vapor pressure ratio of the complexes is $p(\text{KYCl}_4)/p(\text{KScCl}_4) = 8.71$, $p(\text{KLaCl}_4)/p(\text{KYCl}_4) = 2.62$, and $p(\text{KYCl}_4)/p(\text{KNdCl}_4) = 2.06$ at 1 300 K. While the vapor pressure ratios are $p(\text{ScAl}_2\text{Cl}_9)/p(\text{YAl}_2\text{Cl}_9) = 3.13$, $p(\text{YAl}_2\text{Cl}_9)/p(\text{LaAl}_3\text{Cl}_{12}) = 1.64$, $p(\text{YAl}_2\text{Cl}_9)/p(\text{NdAl}_3\text{Cl}_{12}) = 1.83$ and $p(\text{YAl}_2\text{Cl}_9)/p(\text{SmAl}_3\text{Cl}_{12}) = 1.09$ at 1 300 K calculated from the thermodynamic data of the complexes LnAl_nCl_{3n+3} obtained by WANG^[5]. So, the difference of formation ability between the vapor complexes KScCl₄, KYCl₄ and KLnCl₄ is larger than that between ScAl_nCl_{3n+3}, YAl_nCl_{3n+3} and LnAl_nCl_{3n+3}, though ScAl_nCl_{3n+3} and YAl_nCl_{3n+3} possess different form from LnAl_nCl_{3n+3} within the same temperature range.

The values of pressure ratios mentioned above indicate that the formation ability of vapor complexes KLnCl₄ is in the order of Y > Sc, Y < La and Y > Nd, which is different from the results in Nd > Y in this study. This is not surprising when considering the selective chlorination in SC-CVT. According to the thermochemical data^[19], the equilibrium constant ratio of the carbonthermic reduction-chlorination subreaction (1), $K_1(\text{Sc})/K_1(\text{Y})$, decreases from 1.4×10^{-4} at 1 300 K to 2.1×10^{-6} at 800 K, and the equilibrium constant ratio of the carbonthermic reduction-chlorination subreaction (1) for Y₂O₃ and Ln₂O₃, $K_1(\text{Y})/K_1(\text{Ln})$, which is equivalent to the equilibrium constant of the exchange subreaction (2), is equal to 1.8×10^{-10} for Y-La, 2.63×10^{-7} for Y-Nd and 1.24×10^{-5} for Y-Sm at 800 K and 1.50×10^{-6} for Y-La, 1.22×10^{-3} for Y-Nd and 3.57×10^{-3} for Y-Sm at 1 300 K, respectively. That is, the chlorides amount changes as YCl₃ > ScCl₃, YCl₃ < LaCl₃, YCl₃ < NdCl₃ and YCl₃ < SmCl₃. Our experiment also shows that the selective chlorination of the raw materials with dry Cl₂ gas at 800 K for 2 h may result in an yield of 80% for YCl₃; while Sc₂O₃ is hardly to chlorinate, and the chloride yield ratios are 1.73 for La:Y, 2.40 for Nd:Y and 1.59 for Sm:Y, respectively. This agrees with the results in this study.

Furthermore, the total transported yield shows that the SC-CVT transport ability is Y > Sc, La > Y, Nd > Y and Sm > Y in this study. But the stability order of these gaseous rare earth complexes is also demonstrated both by the SC-CVT transport yield of their pure oxides, Y > Sc, Y > La, Y > Nd and Y >

Sm by previous paper mediated by $\text{KLnCl}_4^{[20]}$, and $\text{Sc} > \text{Y} > \text{La}$ obtained by Adachi et al^[6] from their binary oxide mixtures mediated by KLnCl_4 using CVT reaction. The total transported yield ratios between YCl_3 and lanthanide chlorides in the individual oxides are 1.48 for $\text{YCl}_3\text{:ScCl}_3$, 6.25 for $\text{YCl}_3\text{:LaCl}_3$, 2.01 for $\text{YCl}_3\text{:NdCl}_3$ and 1.55 for $\text{YCl}_3\text{:SmCl}_3$ mediated $\text{KLnCl}_4^{[20]}$. From the binary oxide mixtures, however, it is 128.80 for $\text{YCl}_3\text{:ScCl}_3$, while only 1.62 for $\text{LaCl}_3\text{:YCl}_3$, 1.16 for $\text{NdCl}_3\text{:YCl}_3$ and 1.26 for $\text{SmCl}_3\text{:YCl}_3$ in this study. This might be explained by the much lower carbonthermic reduction-chlorination ability of Y_2O_3 than the lanthanide oxides in binary systems, which is very important in the selective reaction. The selective reaction results in different SC-CVT characteristics of the binary oxide mixtures from their individual oxides.

REFERENCES

- [1] Boghosian S, Papatheodorou G N. Handbook on the Physics and Chemistry of Rare Earths, Vol. 23 [M]. Jr Gschneidner K A, Eyring L eds. Amsterdam: Elsevier Science B V, 1996.
- [2] JIANG Jiar-zhuang, Ozaki T, Machida K, et al. Separation and recovery of rare earths via a dry chemical vapor transport based on halide gaseous complexes[J]. J Alloys Comp, 1997, 260(2): 222 - 235.
- [3] WANG Zhi-chang, WANG Lin-shan, GAO Rong-jie, et al. Formation thermodynamics of the rare earth vapor complexes[J]. J Chem Soc Faraday Trans, 1996, 92(10): 1887 - 1891.
- [4] WANG Zhi-chang, WANG Lin-shan. Thermodynamic properties of the rare earth element vapour complexes $\text{LnAl}_3\text{Cl}_{12}$ from $\text{Ln} = \text{La}$ to Lu [J]. Inorg Chem, 1997, 36(8): 1536 - 1541.
- [5] WANG Lin-shan. Thermodynamic Properties of the Rare Earth Elements Vapor Complexes $\text{LnAl}_n\text{Cl}_{3n+3}$ [D]. Shenyang: Northeastern University, 1997. (in Chinese)
- [6] Adachi G, Murase K, Shinozaki K, et al. Mutual separation characteristics for lanthanoid elements via gas phase complexes with alkaline chlorides[J]. Chem Lett, 1992, 244(4): 511 - 514.
- [7] Murase K, Shinozaki K, Machida K, et al. Mutual separation characteristics and mechanism for lanthanoid elements via gas phase complexes with alkaline metal and/or aluminium chlorides[J]. Bull Chem Soc Jpn, 1992, 65(10): 2724 - 2728.
- [8] Murase K, Shinozaki K, Hirashima Y, et al. Rare earth separation using a chemical vapour transport process mediated by vapour complexes of the $\text{LnCl}_3\text{-AlCl}_3$ system[J]. J Alloys Comp, 1993, 198(1): 31 - 38.
- [9] WANG Zhi-chang, YU Jin, YU Yong-li. Comparative study of the mutual separation characteristics and mechanism for neighboring rare earth elements from binary chloride mixtures and oxide mixtures via vapour complexes[J]. Bull Chem Soc Jpn, 1996, 69(8): 2369 - 2374.
- [10] WANG Zhi-chang, SUN Yan-hui. A stepwise selective chlorination-chemical vapour transport reaction for rare earth separation[J]. Chem Lett, 1997, 309(10): 1113 - 1114.
- [11] SUN Yan-hui, WANG Zhi-chang, GUO Lei. Mutual separation characteristics of neighboring rare earth elements Nd, Sm, Eu and Gd using stepwise chlorination-chemical vapor transport[J]. J Alloys Comp, 1998, 269(1): 88 - 91.
- [12] JIANG Jiar-zhuang, Ozaki T, Machida K, et al. Mutual separation characteristics for the scandium, yttrium and lanthanum with chemical vapor transport process mediated by metal chloride gaseous complexes[J]. J Alloys Comp, 1998, 264(2): 157 - 163.
- [13] SUN Yan-hui, ZHANG Li-qing, LEI Peng-xiang, et al. Stepwise chlorination-chemical vapor transport reaction for rare earth oxide mixtures $\text{Gd}_2\text{O}_3\text{-Tb}_4\text{O}_7$, $\text{Tb}_4\text{O}_7\text{-Dy}_2\text{O}_3$, and $\text{Dy}_2\text{O}_3\text{-Ho}_2\text{O}_3$ [J]. J Alloys Comp, 2002, 335(2): 196 - 199.
- [14] SUN Yan-hui, ZHANG Li-qing, WANG Zhi-chang, et al. A comparative study of mutual separation characteristics for binary mixed oxides $\text{Y}_2\text{O}_3\text{-Ln}_2\text{O}_3$ ($\text{Ln} = \text{Sc, La, Nd}$ and Sm) using stepwise chlorination-chemical vapour transport reaction mediated by vapor complexes $\text{LnAl}_n\text{Cl}_{3n+3}$ [J]. J Alloys Comp, 2000, 306(1): 146 - 150.
- [15] Murase K, Machida K, Adachi G. Vapour phase extraction and mutual separation of rare earths from monazite using CVT mediated by vapour complexes[J]. Chem Lett, 1994, 249(9): 1297 - 1301.
- [16] Murase K, Machida K, Adachi G. Recovery of rare metals from scrap of rare earth intermetallic material by chemical vapour transport[J]. J Alloys Comp, 1995, 217(1): 218 - 225.
- [17] Gschneidner K A Jr. Systematics and anomalies[J]. J Alloys Comp, 1993, 192(1): 1 - 10.
- [18] Mcphail D S, Hocking M G, Jeffes J H E. Thermodynamic considerations of metal halide vapor complexes [J]. J Mater Sci, 1985, 20(2): 449 - 456.
- [19] Knacke O, Kubaschewski O, Hesselmann K. Thermochemical Properties of Inorganic Substances, 2nd ed [M]. Berlin: Springer-Verlag, 1991.
- [20] SUN Yan-hui, HE Peng, TANG Guo-zhang, et al. A comparative study of stepwise chlorination-chemical vapor transport characteristics for pure rare earth oxides [J]. J Chinese Rare Earth Soc, 2002, 20(Spec. Issue): 147 - 150. (in Chinese)

(Edited by YANG Bing)