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A systemic study of stepwise chlorination-chemical vapor transport characteristics of pure rare earth oxides from Sc_2O_3 to Lu_2O_3 mediated by alkaline chlorides as complex former

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Abstract

A systematic study has been carried out for the stepwise chlorination-chemical vapor transport (SC-CVT) characteristics of pure rare earth oxides from Sc_2O_3 to Lu_2O_3 mediated by the vapor complexes $KLnCl_4$ and $NaLnCl_4$ (Ln = Sc, Y and La–Lu) used NaCl and KCl as complex former, respectively. The results showed that the SC-CVT characteristics are similarly for NaCl and KCl as complex former, the main deposition temperature of the rare earth chlorides $LnCl_3$ is in the increasing order $ScCl_3 < YCl_3 < LaCl_3$, and then with a systematically decreasing trend from the early lanthanide chlorides to the end one. The results also showed that the total transported amount of the produced chlorides is $YCl_3 > ScCl_3$, and they are much higher than that of most lanthanoid chlorides. For lanthanoids, the total transported amount of chloride increases systematically from the early lanthanoid chlorides to the end one except for $EuCl_3$ and $GdCl_3$ mediated by KCl and NaCl as complex former, respectively, which showed the divergence effect of Gd in the total transport efficiency. But there are some differences in SC-CVT characteristics of pure rare earth oxide mediated by KCl and NaCl as complex former, that is the main deposition temperature region for the same rare earth element was lower for KCl than that for NaCl as complex former except for $LaCl_3$, $CeCl_3$, $YbCl_3$ and $LuCl_3$, while the total transport amount of rare earth chloride for KCl as complex former is higher than that for NaCl except for $LaCl_3$ and $EuCl_3$. More over, the discussion was carried out for Sc and Y on the one hand and the lanthanides contain 4f electron as another hand based on the 4f electron hybridization assumption. Further more, the transport characteristics of rare earth oxides with alkaline chlorides as complex former in this study were compared to that with $AlCl_3$ as complex former.

Keywords: Rare earth compounds; Liquid–liquid reactions; Thermodynamic properties

1. Introduction

Rare earth chlorides with lower volatility can react with the aluminum chlorides or alkaline chlorides forming the vapor complexes such as $LnAl_nCl_{3n+3}$ [1] or $ALnCl_4$ [2] (Ln = rare earth elements, A = alkaline elements, $n = 1–4$). Mutual separation of rare earth elements or preparation of pure rare earth chlorides from the mixed oxides [3–12], chlorides [3,11], crude ore [13] or scrap of rare earth materials [14] mediated by the vapor complexes mentioned above used by chemical vapor transportation (CVT) or stepwise selective chemical vapor transportation (SC-CVT) have been carried out intensively by Adachi's group [1–8,12–14] and Wang's group [9–11]. The results showed that the separation efficiency or the transported yields of rare earth chlorides are higher mediated by the vapor complexes $ALnCl_4$ than that by $LnAl_nCl_{3n+3}$. However, the CVT laws of the rare earth vapor complexes for different complex former are unknown clearly up to now, and the data for separation efficiency and transported yields of rare earths are experiential, that means we lack of the complete set of experimental data of thermodynamic properties of the rare earth vapor complex except that for $LnAl_nCl_{3n+3}$. Recently, Adachi's group investigated the CVT laws of lanthanoid chlorides from La to Lu mediated by $AlCl_3$ as complex former for 1 h, the results showed that the total transported yield for lanthanoid chloride is increasing with the lanthanoid contraction except for $EuCl_3$ [4]. Similarly, Wang's group reported the CVT laws of Sc_2O_3, Y_2O_3 and La_2O_3–Lu_2O_3 used $AlCl_3$ as the complex former through

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by SC-CVT [15]. The results showed that both the transported yields and the main deposition temperature region for Sc_2O_3 and Y_2O_3 are not relative to their ionic radii, while the lanthanoid elements show the Gd divergence effect both in the transported yields and in the main deposition temperature region.

On the other hand, Wang's group has determined the thermodynamic properties of the gaseous species $LnAl_nCl_{3n+3}$ ($n = 1$–4) for all of rare earth elements including Sc and Y, and found that $LnAl_3Cl_{12}$ is the predominant gaseous complex species for the lanthanoid series from La to Lu [16] while $LnAl_2Cl_9$ for Sc and Y [17] in the temperature range from 500 to 900 K.

More over, systematic analysis has been carefully carried out for physical and chemical properties of rare earth complexes in the solid and liquid states since the early 1950 s. In particular, Gschneidner [18] recently represented them as functions of metallic or ionic radius from Sc to Lu and introduced a 4f electron hybridization assumption to explain the systematics and anomalies.

From mentioned above, neither the CVT laws nor the thermodynamics properties of rare earth vapor complexes $ALnCl_4$ mediated by alkaline chlorides as complex former are investigated systematically from Sc to Lu. Thus, in this study, we tried to systematic investigate the stepwise chlorination-chemical vapor transport reaction characteristics for Sc_2O_3, Y_2O_3 and La_2O_3–Lu_2O_3 (except Pm) mediated by KCl and NaCl as complex former, respectively, and then explain the systematics and anomalies by the assumption of 4f electron hybridization of Gschneidner [18].

2. Experimental details

The chemicals used in this study were analytical purity for KCl, NaCl, active carbon powder and ≥ 99.9% purity for all rare earth oxides and $Ce(CO_3)_2$. A raw mixture was formed by mixing active carbon and KCl or NaCl with a pure rare earth oxide at an atomic ratio of C:Ln:K (or Na) = 3:1:1, which contains about 5.0 mmol of each rare earth element.

The SC-CVT reaction was carried out in a cylindrical alumina reactor tube, 25 mm inner diameter and 1000 mm length as described in previous paper [9–11,15], with a given temperature gradient showed in Fig. 1. Let T denote the highest temperature in the tube reactor, where the raw materials were placed. The raw material was chlorinated by dry Cl_2 gas with a flow rate of 20 $cm^3\ min^{-1}$ at $T = 800$ K for 2 h. The Cl_2 gas was replaced by a dry Ar-Cl_2 mixed gas with the flow rates of 30 and 10 $cm^3\ min^{-1}$, respectively, within the temperature range of $T = 800$–1300 K. Then, the rare earth chlorides reacted with KCl or NaCl to form the vapor complexes $KLnCl_4$ or $NaLnCl_4$, which were transported chemically along the temperature gradient in the tube reactor at $T = 1300$ K for 6 h with the Ar–Cl_2 with the flow rates of 30 and 10 $cm^3\ min^{-1}$ as carrier gas. At the end of each run, the amount of the rare earth chlorides produced was determined from the peak intensity of the characteristic bands (nm)—Sc^{3+}: 361.395, Y^{3+}: 324.228, La^{3+}: 408.672, Ce^{3+}: 418.660, Pr^{3+}: 414.311, Nd^{3+}: 430.358, Sm^{3+}: 442.434, Eu^{3+}: 412.970, Gd^{3+}: 342.247, Tb^{3+}: 350.917, Dy^{3+}: 353.170, Ho^{3+}: 339.898, Er^{3+}: 337.271, Tm^{3+}: 313.126, Yb^{3+}: 328.397, Lu^{3+}: 261.542, on an inductively coupled plasma atomic emission spectrometry (Perkin–Elmer, Optima 2000).

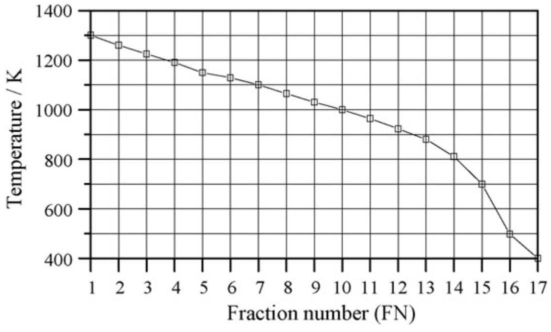

Fig. 1. The temperature gradient curve used in this study.

3. Results and discussion

3.1. The mechanism of SC-CVT reaction

The SC-CVT reaction mechanism might mainly be a combination of carbonthermic reduction–chlorination subreaction of the rare earth oxides at $T = 800$ K:

$$\tfrac{1}{2}Ln_2O_3(s) + \tfrac{3}{2}C(s) + \tfrac{3}{2}Cl_2(g) = LnCl_3(s) + \tfrac{3}{2}CO(g)$$
$$(Ln = Sc,\ Y,\ La,\ Nd,\ Sm,\ Eu,\ Gd\ and\ Dy\text{–}Lu) \qquad (1)$$

$$Ce(CO_3)_2(s) + C(s) + \tfrac{3}{2}Cl_2(g) = CeCl_3(s) + 3CO_2(g) \qquad (2)$$

$$\tfrac{1}{6}Pr_6O_{11}(s) + \tfrac{11}{6}C(s) + \tfrac{3}{2}Cl_2(g) = PrCl_3(s) + \tfrac{11}{6}CO(g) \qquad (3)$$

$$\tfrac{1}{4}Tb_4O_7(s) + \tfrac{7}{4}C(s) + \tfrac{3}{2}Cl_2(g) = TbCl_3(s) + \tfrac{7}{4}CO(g) \qquad (4)$$

complex formation subreactions of the produced chlorides at $T = 1300$ K:

$$LnCl_3(l) + ACl(l) = ALnCl_4(g)$$
$$(A = K\ and\ Na,\ Ln = Sc,\ Y\ and\ La\text{–}Lu) \qquad (5)$$

and the CVT subreactions of the vapor complexes $ALnCl_4$ along the temperature gradient:

$$ALnCl_4(g) = LnCl_3(l\ or\ s) + ACl(s\ or\ l)$$
$$(A = K\ or\ Na,\ Ln = Sc,\ Y\ and\ La\text{–}Lu) \qquad (6)$$

The total transported amount of $LnCl_3$ would mainly be determined by the gas–solid reaction (1)–(4) and liquid–liquid reaction (5), while the distribution characteristics of $LnCl_3$ in the reactor tube would mainly be determined by the vapor complexes selective CVT subreactions (6) along the temperature gradients.

3.2. The deposition of the rare earth chlorides

Fig. 2 show the SC-CVT reaction results of the pure oxide from Sc_2O_3 to Lu_2O_3 in the form of deposition profiles for the rare earth chlorides produced versus fraction numbers (FN) of the receptors, taking KCl and NaCl as complex former and Argon gas as carried gas in the given temperature gradient for 6 h. Fig. 3 show the SC-CVT reaction results of the pure oxide in the form of main deposition temperature region for the rare earth chlorides transported with the larger amounts versus atomic numbers of the rare earth elements from La to Lu determined in this study, for comparison, together with the results of $LnCl_3$ mediated by $LnAl_nCl_{3n+3}$ in the previous paper [15].

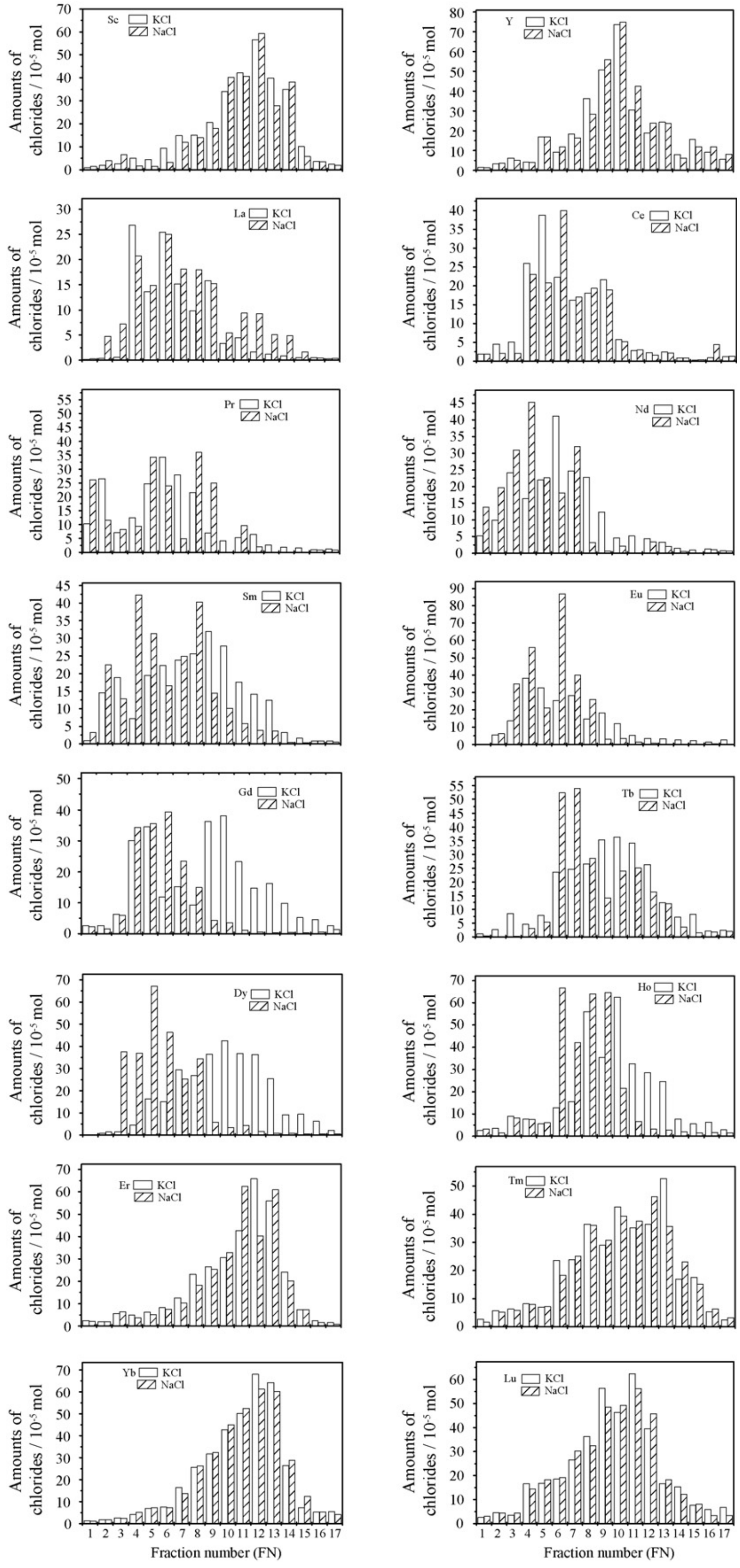

Fig. 2. Distribution of rare earth chlorides deposits in a SC-CVT reaction formed from their pure oxides mediated by the vapor complexes $NaLnCl_4$ and $KLnCl_4$.

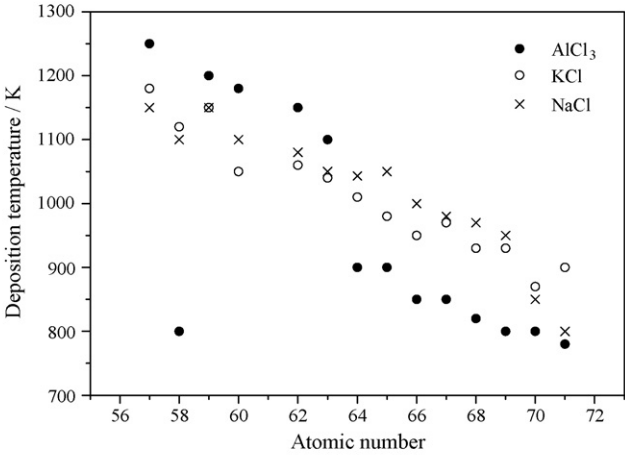

Fig. 3. The main deposition temperature of the largest amounts of lanthanoid chlorides formed from the pure oxides La_2O_3–Lu_2O_3 vs. the atomic number of each rare earth elements in SC-CVT reaction.

It can be seen that the SC-CVT characteristics of pure rare earth oxides are similarly for NaCl and KCl as complex former, the main deposition temperature of the transported chlorides with the larger amounts is in a systematically decreasing trend from the early lanthanoid chlorides to the end one. The results indicated that the low stability of the early lanthanoid vapor complexes $ALnCl_4$ (A = K and Na) even at the higher temperature, while the higher stability of the end one in the higher and middle temperature ranges. In another words, the stability of the vapor complexes $ALnCl_4$ is increasing with the decreasing of the ionic radius of rare earth element, and have been transported more easily to the lower temperature region and decomposed into ACl and $LnCl_3$. This is the same as that for $LnAl_nCl_{3n+3}$ used $AlCl_3$ as complex former [4,15]. These arguments would be supported by the results in the mutual separation of mixed rare earth oxides mediated by $KLnCl_4$, too [19–22].

Compared the deposition temperature of $LnCl_3$ mediated by KCl and NaCl as complex former, it can be found that the main deposition temperature of $LnCl_3$ is relatively lower for KCl as complex former than that for NaCl as complex former, which showed that the stability of $KLnCl_4$ is higher than that of $NaLnCl_4$ at the experimental temperature region for the same rare earth except for La, Ce, Yb and Lu. The exceptive result of La, Ce, Yb and Lu may be have relevant to their exceptive ionic structure and electron configuration of $[Xe]4f^0$ for La^{3+}, $[Xe]4f^1$ for Ce, $[Xe]4f^{13}$ for Yb and $[Xe]4f^{14}$ for Lu, which are nearly empty or full state for the 4f electron orbit, but can not be explained from thermodynamic because lack of the data up to now.

In addition, the radius of Sc^{3+} is the smallest of rare earth trivalent ion and the radius of Y^{3+} is nearly that of the Ho^{3+} and Er^{3+}. However, the SC-CVT determinations in this study show both the difference between Sc_2O_3 and Y_2O_3 on the one hand and the lanthanoid oxides on the other hand. From Fig. 2, the results showed that the main concentrated temperature region is 1000–800 K (FN = 10–14) for $ScCl_3$, 1080–980 K(FN = 8–11) for YCl_3 while 1200–1020 K (FN = 4–9) for $LaCl_3$, 1120–1000 K (FN = 6–10) for $HoCl_3$ and 1020–800 K (FN = 9–14) for $ErCl_3$ whether KCl or NaCl as complex former. The concentrated temperature should be the lowest for $ScCl_3$ because the largest volatility of $ScCl_3$ and the smallest ionic radius of Sc^{3+}, but the experiment result is not such case. While the deposited temperature of YCl_3 is relatively higher than that of $HoCl_3$ and $ErCl_3$, which indicated that Sc and Y have different CVT characteristics compared with lanthanoids, and these are similar with that of $AlCl_3$ as complex former [15] and similar to the distribution of $ScCl_3$ and YCl_3 in the mixed oxides using SC-CVT reaction mediated by KCl as complex former [19–22]. Both in the mutual separation for binary mixed oxides Y_2O_3–Ln_2O_3 (Ln = Sc, La, Nd and Sm) [19], Ho_2O_3–Ln_2O_3 (Ln = Sc, La, Nd and Sm) [20], Er_2O_3–Ln_2O_3 (Ln = Sc, Y, La, Nd, Sm, Gd and Ho) [21] and ternary oxides Y_2O_3–Ho_2O_3–Er_2O_3 [22] using SC-CVT reaction mediated by KCl as complex former, the main deposition temperature region of $ScCl_3$ and YCl_3 in the receptor showed exceptive according to their ionic radii comparative with that of the lanthanoid elements. Thus, we can design the furnace with the corresponding temperature gradient to separate or purify the rare earth mixture or rare earth crude oxides.

From Fig. 3, it would be interesting to point out that the deposition temperature of the lighter rare earths are lower for KCl and NaCl as complex former than that for $AlCl_3$ as complex former, while higher for heavier rare earth for KCl and NaCl as complex former, and the turning point presented at Gd element. It indicated that the decomposition temperature of lighter vapor complexes $ALnCl_4$ are lower than that of $LnAl_nCl_{3n+3}$, that is the stability of lighter rare earth vapor complexes $ALnCl_4$ is higher than that of $LnAl_nCl_{3n+3}$ at higher temperature region, and the vise case for the heavier rare earth vapor complexes. This phenomena can be explained from the data of reaction enthalpy Δ_rH_{298} and entropy Δ_rS_{298} of the complex reaction of $(n/2)$ Al_2Cl_6 (g) + $LnCl_3$ (l) = $LnAl_nCl_{3n+3}$ (g) and $LnCl_3$ (l) + ACl (l) = $ALnCl_4$ (g) (A = K and Na). The data of reaction enthalpy Δ_rH_{298} of the former reaction indicated that the complex reaction formed the vapor complex $LnAl_nCl_{3n+3}$ is an endothermic reaction while the latter one is an exothermic reaction. On the one hand, the change of Gibbs free energy of the reaction Δ_rG_T at the reaction temperature are decreasing both for $LnAl_nCl_{3n+3}$ and $ALnCl_4$ from La to Lu although the data for $ALnCl_4$ are not complete for each rare earth elements, and the value of Δ_rG_T for $ALnCl_4$ is more negative than that of $LnAl_nCl_{3n+3}$ for the same element, so the lighter rare earth complex $ALnCl_4$ is more stable than that of $LnAl_nCl_{3n+3}$ and the main deposition temperature region is lower than that of $LnAl_nCl_{3n+3}$. On the other hand, the heavier rare earth complex is more stable than the lighter one both for $ALnCl_4$ and $LnAl_nCl_{3n+3}$, only because the complex reaction of $ALnCl_4$ is an exothermic reaction and it more easily decomposed at higher temperature than that of $LnAl_nCl_{3n+3}$. That may be the reason of the lighter and heavier rare earths gave the opposite phenomena in the distribution of $LnCl_3$ mediated by $AlCl_3$ and ACl as complex former, respectively.

3.3. The total transported amounts of chlorides

Fig. 4 show the total transported amounts of chlorides formed from the pure oxides La_2O_3–Lu_2O_3 mediated by KCl and NaCl

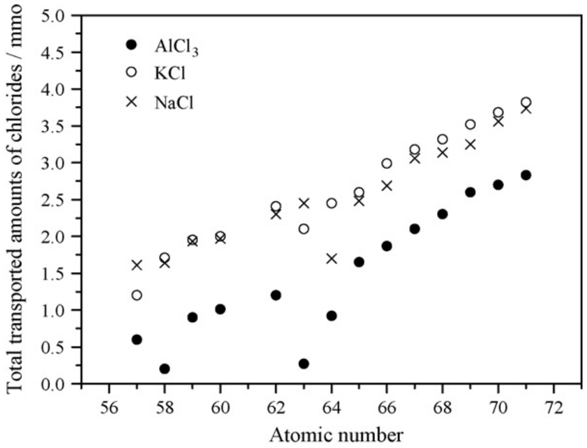

Fig. 4. The total transported amounts of chlorides formed from the pure oxides La_2O_3–Lu_2O_3 vs. the atomic number of each rare earth elements.

s complex former versus the atomic number of each rare earth element. It can be seen that the total transported amount of the produced chlorides increases systematically from the early lanthanoid chlorides to the end one except for $EuCl_3$ and $GdCl_3$ when KCl and NaCl used as complex former, respectively. This proved the rule that the stability of rare earth vapor complexes $ALnCl_4$ increase with the lanthanoid conduction except for Eu and Gd showing the irregularity, that means the stability of rare earth vapor complexes $ALnCl_4$ versus the atomic number of the rare earth elements present Gd divergence effect, which is the same as the rule of physical and chemical properties for the solid or liquid complexes versus the atomic number of the rare earth elements. More over, the total transported amounts of chlorides mediated by KCl as complex former is a little higher than that of NaCl as complex former except for $LaCl_3$ and $EuCl_3$.These results can be explained from the data of reaction enthalpy Δ_rH_{298} and the entropy Δ_rS_{298} of ACl (l) + $LnCl_3$ (l) = $ALnCl_4$ (g) at 298 K. Here, suppose the reaction enthalpy Δ_rH_{298} and the entropy Δ_rS_{298} are not change with the change of temperature, we can calculate the change of Gibbs free energy of the reaction Δ_rG is: −102.6 kJ/mol for $NaLaCl_4$ [23], −101.9 kJ/mol [23] or −68.6 kJ/mol [24] for $KLaCl_4$ at 1300 K, so, the total transported amounts of $LaCl_3$ is larger for NaCl as complex former than that for KCl as complex former. Furthermore, the Gibbs free energy for the reaction forming the vapor complexes $ALnCl_4$ can be calculated from literature [25,26], the value is −57.1 kJ/mol for $NaNdCl_4$ [25], −112 kJ/mol (1000 K) for $NaHoCl_4$ [25], −61.6 kJ/mol for $NaErCl_4$ [25], while −59.8 kJ/mol for $KNdCl_4$ [26], −117 kJ/mol (1000 K) for $KHoCl_4$ [26], −61.7 kJ/mol [23] or −60.5 kJ/mol [24] for $KErCl_4$, respectively. It can be found that the value of the Gibbs free energy of the reaction $LnCl_3$ (l) + NaCl (l) = $NaLnCl_4$ (g) is little higher than that of $LnCl_3$ (l) + KCl (l) = $KLnCl_4$ (g) and indicate that the vapor complexes $KLnCl_4$ is more easily formed and transported than $NaLnCl_4$. But for the same complex former such as NaCl or KCl, the order of transported amounts of different lanthanoid chlorides are not agree with the value of the Gibbs free energy of the corresponding vapor complexes. These might be cannot give the right reason because lacking of the perfect thermodynamic data of the vapor complexes, or the data were presented by different experiment method by different investigator [23–26]. However, the total transported amounts of the chlorides in this study were related to the rare earth chlorides and ACl complex reaction as well as the chlorination ability of the rare earth oxides and the volatility of the produced chlorides.

For comparison, the total transported amounts of chlorides mediated by the $AlCl_3$ as complex former were showed in the Fig. 4 too [15]. The results showed that the total transported amounts of chlorides are higher mediated by the NaCl or KCl as complex former than that mediated by $AlCl_3$. This can be explained as that on the one hand the Gibbs free energy of the reaction of Al_2Cl_6 (g) + $LnCl_3$ (l) = $LnAl_nCl_{3n+3}$(g) (n = 1–4) [16,17] is much higher than that of reaction of $LnCl_3$ (l) + ACl (l) = $ALnCl_4$ (g) [23–26], that means the forming ability of the complex $LnAl_nCl_{3n+3}$ is more weak than that of $ALnCl_4$. On the other hand, the complex reaction of Al_2Cl_6 and $LnCl_3$ taken place on the surface of the $LnCl_3$ melts and attributed to the gas–liquid reaction, while the reaction of ACl and $LnCl_3$ taken place in the inner parts of the melts and attributed to the liquid–liquid reaction. From dynamics, the latter reach balance more easily.

On the other hand, the total transported amounts of $CeCl_3$ did not present exceptive value relative the atomic number and $EuCl_3$ and $GdCl_3$ is a little lower than the neighboring elements mediated by KCl and NaCl, respectively in this study, while the $CeCl_3$ and $EuCl_3$ are remarkable lower than that of others used $AlCl_3$ as complex former [15], which are much lower than that used KCl and NaCl as complex former. These experimental results may be explained as there are transform valance for Ce and Eu, and the electron configuration of the atom is described as $[Xe]4f^1 5d^1 6s^2$ for Ce and $[Xe]4f^7 6s^2$ for Eu and easily form Ce^{4+} and Eu^{2+} except that Ce^{3+} and Eu^{3+} according to the electron filling rule. It is believed that the lower chlorination ability of CeO_2 at 800 K as well as the produced $CeCl_3$ is easily chlorinated to $CeCl_4$ by the chlorine resulted the lower transported amounts of $CeCl_3$ mediated by $AlCl_3$ as complex former, while $Ce(CO_3)_2$ was used as the raw material in this study, our preliminary experiment indicated that $Ce(CO_3)_2$ did not decompose at 800 K and which chlorination ability is stronger than that of CeO_2 at 800 K. Here, the very low total transported amount of $EuCl_3$ might be described by the very lower stability of $EuCl_3$ than $EuCl_2$ at 1300 K and the very low complex ability of $EuCl_2$ with $AlCl_3$, While the result in this study showed that the complex ability of $EuCl_2$ and KCl or NaCl was much higher than that of $EuCl_2$ and $AlCl_3$ though there are no data for the complex reaction of $EuCl_2$ with KCl or NaCl until to now. The slightly low total transported amount of $GdCl_3$ mediated by $AGdCl_4$ might be explained by the Gd divergence effect shown in the thermodynamic behavior of the vapor complexes. These can be supported by the experimental result of mutual separation of Er_2O_3–Gd_2O_3 by $KLnCl_4$ [21].

In order to represent the systematics and anomalies in the SC-CVT characteristics of pure rare earth oxides from Sc_2O_3, Y_2O_3, La_2O_3–Lu_2O_3, Fig. 5 shows the total transported amount of $LnCl_3$ versus ionic radius of Ln^{3+} with a six-fold coordination number from Ln = Sc to Ln = Lu though the actual structural

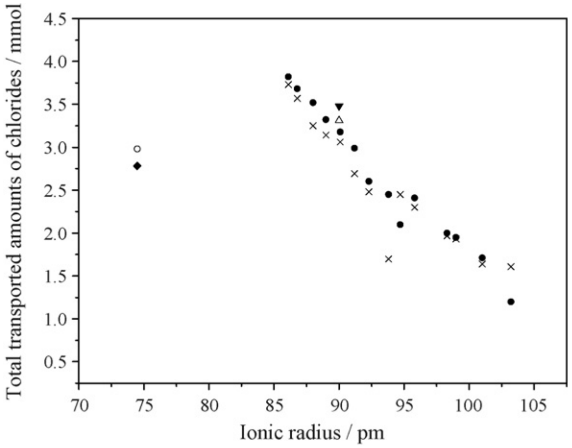

Fig. 5. Total transported amounts of chlorides formed from the pure oxides Sc_2O_3, Y_2O_3, La_2O_3–Lu_2O_3 vs. the ionic radius of each rare earth elements. ●: La–Lu, □: Sc, Δ: Y, KCl as complex former; × : La–Lu, ♦: Sc, ▼: Y, NaCl as complex former.

information is lacking for the vapor complexes $ALnCl_4$ at 1300 K except that only the assumption of C_{2v} type structure for $KNdCl_4$ proposed by Adachi [12]. It can be seen from Fig. 5 that the produced $ScCl_3$ and YCl_3 are much larger than that of most of lanthanoid chlorides both mediated by KCl and NaCl as complex former. Here, the total transported amount of $ScCl_3$ is 2.80×10^{-3} mol and YCl_3 is 3.48×10^{-3} mol mediated by $NaLnCl_4$ (Ln = Sc and Y), and $ScCl_3$ is 2.98×10^{-3} mol, YCl_3 is 3.37×10^{-3} mol mediated by $KLnCl_4$ (Ln = Sc and Y), and the amounts of transported lanthanide chlorides changed from 1.61×10^{-3} mol for $LaCl_3$ to 3.73×10^{-3} mol for $LuCl_3$ mediated by $NaLnCl_4$ (Ln = La–Lu), and 1.20×10^{-3} mol for $LaCl_3$ to 3.82×10^{-3} mol for $LuCl_3$ mediated by $KLnCl_4$ (Ln = La–Lu), respectively, These difference of Sc and Y from the lanthanides are determined by the nature of Sc and Y, which are prominent in the result that mediated by $AlCl_3$ as complex former and the transported amount of $ScCl_3$ is near that of the heavier rare earth and YCl_3 is larger far from that of each lanthanide chlorides [15].

In nature, Sc^{3+} and Y^{3+} do not contain 4f electron and the configuration are different from that of lanthanides. Gschneider [18] has explained the experiments for various physical and chemical properties of rare earth elements, compounds and complexes in solid and liquid states by using 4f electron hybridization assumption. The assumption is also supported by the recent research that the stability of complexation constant of vapor complexes of $ScAl_2Cl_9$ and YAl_2Cl_9 are much higher than that of $LnAl_3Cl_{12}$ (Ln = La–Lu) by Wang's group [16,17]. Thus the transported amounts of $ScCl_3$ and YCl_3 are much larger than that of lanthanide chlorides and the deposition temperature region are exceptive too in this study.

It is interesting that the transported amounts of lanthanoid chlorides mediated by alkaline chlorides are larger than that by $AlCl_3$ as complex former, while the transported $ScCl_3$ and YCl_3 mediated by KCl or NaCl are lower than that by $AlCl_3$ as complex former. These were approved in the experiment that mutual separation of binary mixed oxides Y_2O_3–Ln_2O_3 (Ln = Sc, La, Nd, Sm) mediated by KCl [19] and $AlCl_3$ [27] as complex former by SC-CVT reaction. On the other hand, the Gibbs free energy of the complex reaction of $LnCl_3$ and ACl in the literature is −121 kJ/mol for $KYCl_4$, −119 kJ/mol for $NaYCl_4$, −61.9 kJ/mol for $KScCl_4$ and −49.3 kJ/mol for $NaScCl_4$ at 1000 K, which indicated that the stability of $AYCl_4$ is higher than that most of $ALnCl_4$ (Ln = La–Lu) and $AScCl_4$ is lower than that most of $ALnCl_4$ (Ln = La–Lu). But then, the stability of the vapor complexes determined not only by the thermodynamics properties but also by the volatility of the pure rare earth chlorides, and the much more volatility of $ScCl_3$ resulted that larger transported amounts than most of the lanthanide chlorides.

Therefore, the separation and purification of rare earths from the mixed oxides or crude ore can be realized by the SC-CVT reaction based on the remarkable difference of SC-CVT characteristics of different rare earths, especially of Sc and Y, which were proved by the previous paper [20–22,27–29].

4. Conclusion

This paper presents a complete set of experimental data for SC-CVT characteristics of pure rare earth oxides from Sc_2O_3 to Lu_2O_3 mediated by the vapor complexes $KLnCl_4$ and $NaLnCl_4$. The results showed that the deposition temperature region and the total transported amounts of $ScCl_3$ and YCl_3 are exceptive compared with that of lanthanoids. The SC-CVT characteristics of lanthanoid chlorides present the descending tendency in the deposition temperature from La to Lu, and increasing tendency in the transported amounts from La to Lu except for Eu and Gd in this study. More over, the results showed that there are some difference between the SC-CVT characteristics of $KLnCl_4$ and $NaLnCl_4$.

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