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Vapor Phase Extraction and Mutual Separation of Rare Earths from Monazite Using Chemical Vapor Transport Mediated by Vapor Complexes

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Rare earths chlorides (RCl_3), produced by direct chlorination of monazite concentrate or chlorine free crude oxides, were extracted *via* vapor complexes with KCl. The complexes, $RKCl_4(g)$, decomposed along a given temperature gradient, and RCl_3 was selectively deposited in a temperature region 850-990 °C. Other elements such as Th, U, and P in the monazite were concentrated at the lower temperature fractions. Coexistence of vapor complex(es) in a RCl_3-$POCl_3$ system was suggested from the difference between the yields of RCl_3 for the concentrate and the crude oxides.

Various kinds of new functional materials, in which rare earth elements (R) play a key role, have been increasingly developed. At present, purified rare earths for commercial use are produced almost exclusively by means of a wet method. However, the wet method results in high production cost since it requires a series of complicated steps accompanied by dissolution, precipitation, and drying processes. On the other hand, we have reported recently that the mutual separation of rare earth chloride mixtures can be successfully conducted by a complete dry process using a chemical vapor transport (CVT) phenomenon mediated by metal halide vapor complexes of RCl_3-$AlCl_3$[1] and RCl_3-ACl[2] (A, alkali metals) systems. The CVT method is also applicable to the recovery of rare metals from the scrap of intermetallic materials.[3] This technique is based on the difference in the temperature dependencies of formation-decomposition equilibria for these vapor complexes.

In the present work, vapor phase extraction and mutual separation characteristics of rare earths were studied using the concentrate or the crude oxide of monazite as a raw material for the CVT reaction, and the resulting separation efficiency is discussed in terms of the transport reaction conditions and mechanism.

The apparatus employed for the CVT reaction comprises a cylindrical furnace (length 860 mm) made from Kanthal-wound ceramic tube (inner diameter 50 mm), insulating material, fused silica reactor (inner diameter 25 mm, length 1500 mm), and alumina inner tubes used to collect fractions transported by the reaction (Fig. 1). The furnace consists of 16 divided heaters to be independently controlled by thermoregulators so as to produce various temperature gradients along the axis of the reactor. The temperature gradient used for this work is shown in Fig. 1.

Table 1. Composition of a monazite concentrate

Oxide	Content / wt%
Al_2O_3	0.29
SiO_2	1.8
P_2O_5	19
CaO[a)]	1.6
Fe_2O_3	4.1
Y_2O_3[a)]	0.52
ZrO_2	4.4
La_2O_3[a)]	15
CeO_2[a)]	27
Pr_6O_{11}[a)]	4.6
Nd_2O_3[a)]	10
PbO	0.32
ThO_2[a)]	11
U_3O_8	0.39

a) elements a crude oxide from monazite contains.

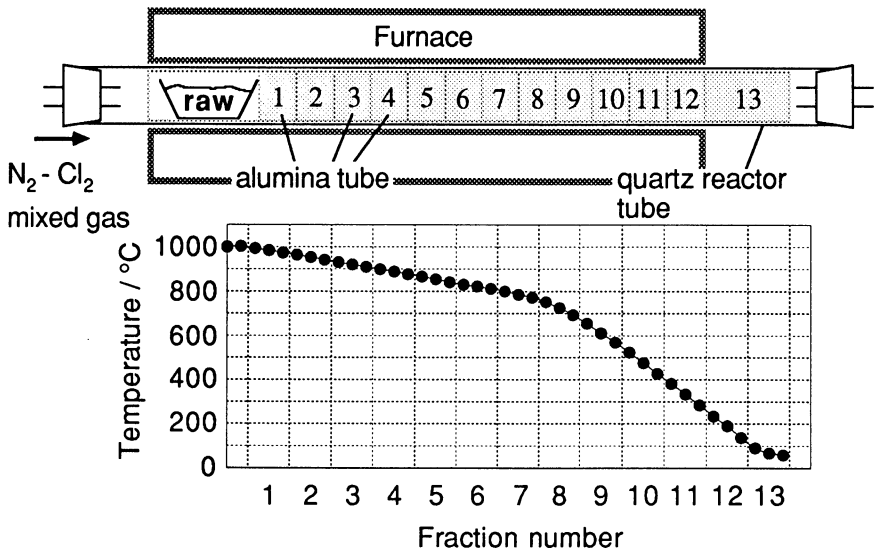


Fig. 1. Assembly of electric furnace for the chemical vapor transport reaction and temperature gradient in the furnace. The figures concerning the furnace denote the fraction numbers (*FN*).

The monazite concentrate (2.93 g, see Table 1), in which the rare earths are contained as phosphate (RPO_4), or crude oxide (R_2O_3, 2.00 g) prepared from the concentrate were used as raw materials; each contains the same amount, 9.4×10^{-3} mol, of rare earths. A small amount of active carbon powder and 4.7×10^{-3} mol of K_2CO_3 (K:R = 1:1) were mixed with the raw material as deoxidant and a precursor of the complex former, KCl, respectively. The use of the precursor K_2CO_3 instead of KCl prevents any deviation of the composition where K:R = 1:1 during the temperature of furnace is raised before initiating the reaction.[4)]

The raw mixture was put on a carbon boat and loaded in the reactor tube with a stream of N_2 gas (30 cm^3 min^{-1}) and, then, the furnace was operated to heat the mixture to 1000 °C. After the temperature gradient (Fig. 1) was attained, Cl_2 (5 cm^3 min^{-1}) was introduced into the reactor to chlorinate the mixture, yielding RCl_3, KCl, and other metal chlorides. The resulting rare earth chlorides were converted to the vapor complexes $KRCl_4$(g) *via* reaction with KCl as

$$RCl_3(s, l) + KCl(s, l) = KRCl_4(g), \quad (1)$$

where (s), (l), and (g) represent solid, liquid, and gas phases, respectively. These complexes were driven with the gas stream along the temperature gradient, decomposed according to the reverse process of Eq. 1, and RCl_3

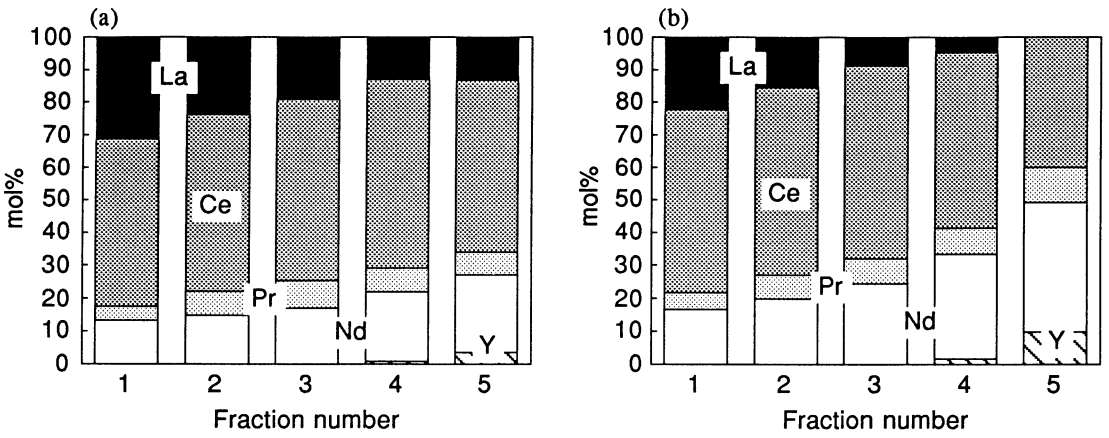


Fig. 2. Composition of rare earths chlorides for the deposits of *FN*=1-5. Raw materials were (a) concentrate and (b) crude oxide of monazite; each contains 9.4×10^{-3} mol of rare earths. Complex former was K_2CO_3 (4.7×10^{-3} mol); reaction time was 84 h.

was regenerated. The other metal chlorides were also vaporized and transported. After the CVT reaction lasted for 82 hours, the resulting deposits along the temperature gradient were collected from the inner tubes.[1-3] Then the deposits were dissolved individually in deionized water to determine the composition of rare earths and other element for each portion (*FN*; fraction numbers) on an X-ray fluorometry.

Rare earth chlorides were deposited mainly in portions of *FN*=1 to 5, in a temperature range 990-830 °C. Figure 2 shows the composition of RCl_3 at these fractions. The chlorides of La, Ce, Pr, Nd, and Y were deposited in order at the given fractions of higher temperature (*FN*=1) to lower one (*FN*=5). The deposition tendency which agrees with the order of ionic radius of rare earths indicates that the vapor complexes of rare earths with a smaller ionic radius are more stable than those with larger ones and prefer to be concentrated at the fractions in the lower temperature region. This result coincides the previous ones for RAl_nCl_{3+3n} vapor complexes.[1]

For the use of both the concentrate and the crude oxides as the raw material, the most part of YCl_3 was condensed at *FN*=5, and the mutual separation of yttrium and other rare earths was carried out satisfactorily. However, $CaCl_2$ whose volatility is quite low also deposited at *FN*=1 to 5 with almost the same deposition profile of rare earths. The residual calcium can be removed after a metallothermal reduction to produce rare earth metal. On the other hand, $ThCl_4$, UCl_4, and the other chlorides (*i.e.* $AlCl_3$, $FeCl_3$, and $ZrCl_4$) were transported to the fractions of lower temperatures than rare earth and calcium chlorides were deposited. A phosphorous compound produced by the chlorination of PO_4^{3-} is condensed mainly at *FN*=13 (< 120 °C); according to a Hartley's work on a high-temperature direct chlorination of monazite based on a thermodynamical aspect,[5] PO_4^{3-} is converted to $POCl_3$. Though $POCl_3$ forms a liquid phase at an ambient temperature, the deposit at *FN*=13 was a yellow solid, which is probably a solid solution of co-deposited $AlCl_3$ and $FeCl_3$.

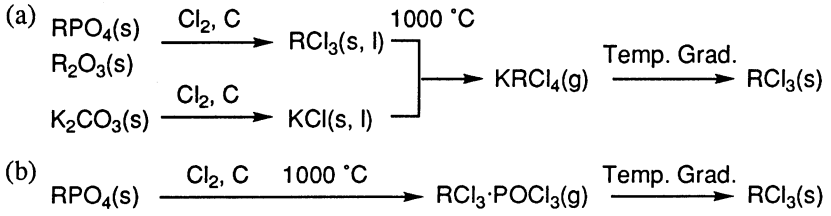
Table 2 summarizes the yields of each RCl_3 except for YCl_3, whose yield was not calculated since the amount of residual YCl_3 on the boat after the reaction for 82 hours was too small to identify by means of X-ray fluorometry. When the complex former KCl (*i.e.* K_2CO_3) was not added the yields, shown as (*c*) and (*d*) in the table, were reduced to about one-half the use of KCl, (*a*) and (*b*). The difference corresponds to the amount of $KRCl_4(g)$ formed. Moreover, the fact that the concentrate provided higher yields than the crude oxide whether KCl are used or not, *i.e.* (*a*) > (*b*) and (*c*) > (*d*), implies that the formation of some vapor species other than $KRCl_4(g)$ concerns to the transport of RCl_3 in addition to $KRCl_4(g)$. The most plausible species are vapor complexes in the RCl_3-$POCl_3$ system because recently it turned out that $POCl_3$ forms high stability oxygen-bridged 1:1 vapor complexes with trivalent and tetravalent chlorides, such as $POCl_3{\cdot}MCl_3(g)$ (M= Al[6, 7] and Gd[7]), $POCl_3{\cdot}M'Cl_4(g)$[8] (M'= Zr and Hf), and in

Table 2. Yields of rare earth chlorides

Raw matrial	KCl	Yield / %				
		La	Ce	Pr	Nd	
concentrate	used	33	63	67	64	(*a*)
crude oxide	used	24	50	53	54	(*b*)
concentrate	not used	17	38	38	36	(*c*)
crude oxide	not used	10	25	27	23	(*d*)
		9	13	14	10	(*a*)-(*b*)
		7	13	11	13	(*c*)-(*d*)
	average	8	13	12.5	11.5	(*e*)
		16	25	29	28	(*a*)-(*c*)
		14	25	26	31	(*b*)-(*d*)
	average	15	25	27.5	29.5	(*f*)

this reaction system the amount of generated $POCl_3$ is at least an equimolar amount with RCl_3. Since the vapor complexes of the RCl_3-$POCl_3$ system have not yet investigated the present CVT mechanism cannot be discussed from the thermodynamic aspect. However, if the complex really forms, the $POCl_3$•RCl_3(g) complex is easier to form than $KRCl_4$(g) because the formation of $POCl_3$•RCl_3(g) is one step reaction (Scheme 1(b)) while the formation of $KRCl_4$(g) needs several steps (Scheme 1(a)).

Differences in the yields, (*a*) - (*b*) and (*c*) - (*d*) as listed in Table 2, correspond to the amount of the "new" vapor complex(es) because the rare earth contents in the concentrate and crude oxide of monazite were unified as 9.4×10^{-3} mol. Similarly, differences in the yields of (*a*) - (*c*) and (*b*) - (*d*) are attributable to the amount of $KRCl_4$(g). Furthermore, the yield obtained on the crude oxides without any addition of KCl, (*d*), represents the amount of RCl_3 transported *via* free RCl_3(g). The differences in the yields of (*a*) - (*b*) and (*a*) - (*c*) give almost the same values as those of (*c*) - (*d*) and (*b*) - (*d*), respectively. From the average values, (*e*) and (*f*), percentages of the generated vapor species, RCl_3(g), $KRCl_4$(g), and the "new" vapor complex(es) are calculated as 37, 43, and 20%, respectively.



Scheme 1.

In conclusion, rare earths were extracted and roughly mutually separated directly from the concentrate or crude oxide of monazite by the combination process of direct chlorination and a CVT reaction *via* the vapor complex $KRCl_4$(g). In case of the concentrate as the raw material, some vapor complex species other than $KRCl_4$(g), probably vapor complexes of the RCl_3-$POCl_3$ system, also effectively act as the mediator for the chemical transport.

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