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Studies on the synergistic extraction of rare earths from nitrate medium with mixtures of *sec*-nonylphenoxy acetic acid and 1,10-phenanthroline

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ABSTRACT

The extraction of rare earths with mixtures of *sec*-nonylphenoxy acetic acid (CA100, H_2A_2) and 1,10-phenanthroline (phen, B) in benzene has been investigated from nitrate medium. The mixtures show synergistic effects on all the selected rare earths, lanthanum, neodymium, samarium, terbium, ytterbium, and yttrium. The extraction stoichiometries of samarium and yttrium with CA100 and its mixtures with phen have been studied in detail with the methods of slope analysis and constant mole. The equilibrium constants and thermodynamic functions are calculated. In addition, the mixtures are proved to have higher selectivity when applied to the separation of the lanthanoids from yttrium compared with single CA100 system.

1. Introduction

As a branch of solvent extraction, synergistic extraction has become a common method for the separation of metal ions. It can not only improve the extraction efficiency and improve the extraction selectivity but also enhance the stability of the extracted complexes, improve the solubility of the extracted complexes in the organic phase, eliminate emulsification and the formation of the third phase, and increase the extraction reaction rate [1]. Mixtures of chelating agents and neutral donors have been extensively used in the synergistic extraction of trivalent lanthanides and actinides [2]. The formation of mixed ligand chelates involving the chelating extractant and adductants such as 1,10-phenanthroline (phen) would provide not only better extractability, but also improved separation [3–8]. Except chelating agents, the extraction of rare earths (REs) with organophosphorus extractants combined with phen has also been studied. For instance, the extraction behavior of REs using a chloroform–kerosine solution containing di-(2-ethylhexyl)phosphoric acid and phen has been reported [9,10]. The stoichiometry, extraction constants and separation factors of REs are determined.

Carboxylic acids have been applied to hydrometallurgical processes, among which *sec*-octylphenoxy acetic acid (CA12) and *sec*-nonylphenoxy acetic acid (CA100) have been recently developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The extraction of REs with CA12 or CA100 has been reported elsewhere [11–18]. Wu et al. [16] have studied the synergistic extraction of yttrium with mixtures of bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex302) and CA100. Sun et al. [17] have investigated the synergistic extraction of some trivalent REs from chloride medium using mixtures of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) and CA100. In our previous work [18], the extraction and separation of REs with CA100 and its mixture with another organophosphoric acid, 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP), have been investigated. The mixtures show decreasing extraction effects with increasing atomic numbers of lanthanoids. The synergistic extraction of lanthanum (III) with the mixtures is studied in detail. The extraction reaction, equilibrium constants, formation constants and thermodynamic parameters are also obtained. Except these three papers, no other work has been reported about the extraction of REs with mixtures containing CA100.

In the present study, the extraction of REs with mixtures of CA100 and phen has been investigated. Effects of aqueous acidity, the ratio of the extractants and experimental temperature are discussed. The selectivity of REs has also been analyzed.

2. Experimental

2.1. Reagents and apparatus

High-purity rare earth oxides (>99.95%) were obtained from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). Stock solutions of REs were prepared by

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dissolving their oxides in concentrated nitric acid and diluting to the required volume with distilled water and then standardized by titration using EDTA standard solution at pH 5.5 with xylenol orange as an indicator. The pH of the aqueous phase was adjusted by the addition of HNO_3 or NaOH solutions. A solution of $NaNO_3$ ($\mu = 0.6\,mol\,L^{-1}$) was used to keep the constant ionic strength. All other reagents were of analytical reagent grade.

CA100 and phen were supplied by Shanghai Rare-Earth Chemical Co., Ltd. and Tianjin Kermel Chemical Reagent Co., Ltd., respectively. Both of the extractants were used without further purification and dissolved in benzene to the required concentrations.

A model pHS-3C digital pH meter was employed for pH measurements (Shanghai Rex Instruments Factory, China).

2.2. Extraction procedures

Equal volumes (4 mL) of aqueous and organic solutions were mixed and shaken for 30 min at 293 ± 1 K unless otherwise stated. After phase separation, the concentrations of REs in the aqueous phase were determined by titration with EDTA, and those in the organic phases were determined by mass balance. All the experimental work was carried out in duplicate and the average result was presented. Distribution ratios (D) were calculated from these concentrations, $D = [RE]_{(o)}/[RE]_{(a)}$.

3. Results and discussion

3.1. Extraction behavior of REs with CA100

The solvent extraction of REs with CA100 in *n*-heptane has been studied earlier, especially the extraction behavior of La^{3+} from chloride medium [18]:

$$La_{(a)}{}^{3+} + 2H_2A_{2(o)} \rightleftharpoons LaHA_{4(o)} + 3H_{(a)}{}^{+} \quad (1)$$

where "a" and "o" represent aqueous and organic phase, respectively.

In Wang et al.'s work [19], the extraction of Eu^{3+} from chloride medium with saponified CA100 in *n*-heptane has been reported:

$$Eu_{(a)}{}^{3+} + 4(NH_4A)_{(o)} \rightleftharpoons EuA_3(NH_4A)_{(o)} + 3NH_{4(a)}{}^{+} \quad (2)$$

In the present study, the extraction of REs with CA100 in benzene from nitrate medium has been investigated. If the extraction of REs is written as follows:

$$RE_{(a)}{}^{3+} + (3-n)NO_{3(a)}{}^{-} + mH_2A_{2(o)} \overset{K_A}{\rightleftharpoons} RE(NO_3{}^{-})_{3-n}H_{2m-n}A_{2m(o)} + nH_{(a)}{}^{+} \quad (3)$$

The relationship between the distribution ratio D_A and the equilibrium constant K_A can be described:

$$\log D_A - n\mathrm{pH} = m\log[H_2A_2]_{(o)} + (3-n)\log[NO_3{}^{-}]_{(a)} + \log K_A \quad (4)$$

Sm^{3+} and Y^{3+} are selected for the extraction tests. The relationship between $\log D_A$ and equilibrium pH values has been studied, giving a straight line with a slope of about 3.0, suggesting that three protons are replaced by one RE ion in the light of cation-exchange mechanism. Accordingly, the plots of $\log D_A - 3\mathrm{pH}$ versus the logarithm of CA100 concentration are linear with a slope of about 2.5. Results are shown in Fig. 1. Therefore, the extraction of Sm^{3+} and Y^{3+} with CA100 in benzene can be expressed as

$$RE_{(a)}{}^{3+} + (5/2)H_2A_{2(o)} \overset{K_A}{\rightleftharpoons} REH_2A_{5(o)} + 3H_{(a)}{}^{+} \quad (5)$$

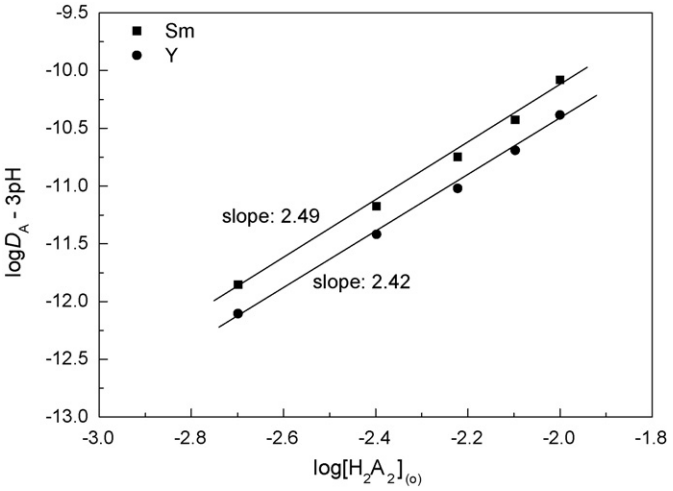

Fig. 1. Effect of CA100 concentration on the extraction of Sm^{3+} and Y^{3+} with CA100. $[RE^{3+}] = 1 \times 10^{-3}\,mol\,L^{-1}$, pH 3.0, and $\mu = 0.6\,mol\,L^{-1}$.

The equilibrium constant, $\log K_A$ for Sm^{3+} and Y^{3+} can be calculated to be −5.2 and −5.4, respectively.

3.2. Synergistic extraction of REs with mixtures of CA100 and phen

In order to gain insight into the synergistic effect of REs observed with mixtures of CA100 and phen, transformation of mole fraction of CA100 (X_{CA100}) experiment has been performed with continuous variation method. When the total concentration of CA100 and phen is fixed at 0.01 mol L^{-1}, the distribution ratios of REs in the mixing system change with changing mole fraction of CA100. According to Xu et al.'s theory [20], the synergistic enhancement coefficient, R, is used to evaluate whether a mixing system has synergistic extraction effect or not:

$$R = \frac{D_{mix}}{D_{CA100} + D_{phen}} \quad (6)$$

The mixtures of CA100 and phen have synergistic effects on all the REs studied in the present work. Table 1 shows the synergistic coefficient values of REs.

As representatives, the synergistic extraction of Sm^{3+} and Y^{3+} has been shown in Fig. 2. It can be seen that the synergistic effects are significant when Sm^{3+} and Y^{3+} are extracted with mixtures of CA100 and phen. If the synergistic extraction of REs from nitrate medium with mixtures of CA100 and phen in benzene is expressed as

$$RE_{(a)}{}^{3+} + (3-i)NO_{3(a)}{}^{-} + xH_2A_{2(o)} + yB_{(o)} \overset{K_{AB}}{\rightleftharpoons} RE(NO_3)_{3-i}H_{2x-i}A_{2x}B_{y(o)} + iH_{(a)}{}^{+} \quad (7)$$

The relationship between D_{AB} and the equilibrium constant K_{AB} can be obtained by

$$\log D_{AB} = x\log[H_2A_2]_{(o)} + y\log[B]_{(o)} + i\mathrm{pH} + \log K_{AB} + (3-i)\log[NO_3{}^{-}]_{(a)} \quad (8)$$

Table 1
Synergistic coefficient of rare earths.

X_{CA100}	R (La)	R (Nd)	R (Sm)	R (Tb)	R (Yb)	R (Y)
0.2	2.2	9.2	12.3	4.1	11.6	7.3
0.4	5.0	21.3	25.3	11.3	19.0	19.0
0.6	3.2	15.7	23.8	8.0	16.8	15.5
0.8	0.8	5.7	8.8	2.5	5.6	2.9

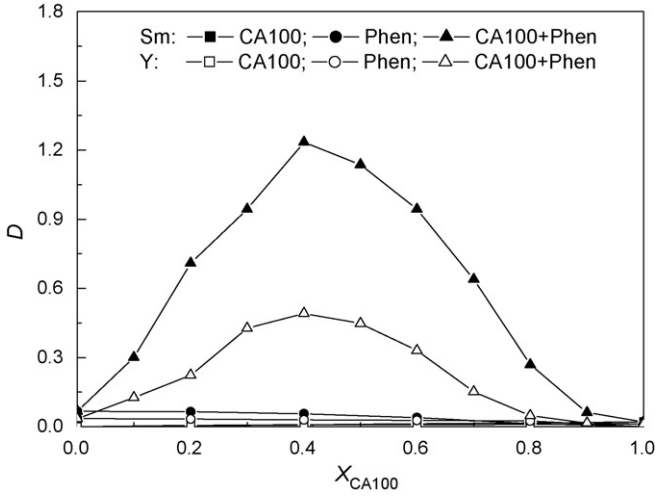

Fig. 2. Synergistic extraction of Sm^{3+} and Y^{3+} with mixtures of CA100 and phen. $[RE^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH 3.0, $\mu = 0.6$ mol L^{-1}, and $C_{CA100} + C_{phen} = 0.01$ mol L^{-1}.

In order to determine the extracted complexes in the mixing system, a series of experiments have been carried out. Firstly, the relationship between D_{AB} and pH were studied at fixed concentrations of CA100 and phen. As shown in Fig. 3, the plots of $\log D_{AB}$ versus pH give a straight line with a slope of about 1.0. Secondly, when the concentration of one extractant is varied at fixed pH value and fixed concentration of the other extractant, the plots of $\log D_{AB} - \mathrm{pH}$ versus the concentration of extractants can also be obtained. Fig. 4 shows the relationship between $\log D_{AB} - \mathrm{pH}$ and $\log[H_2A_2]_{(o)}$ or $\log[B]_{(o)}$ for Sm^{3+} extraction, giving the slope values of about 0.5 and 1.0, respectively. Accordingly, similar results can be obtained for Y^{3+} extraction. Results are shown in Fig. 5. Therefore, the extraction stoichiometry for Sm^{3+} and Y^{3+} can be written:

$$RE_{(a)}{}^{3+} + 2NO_{3(a)}{}^{-} + (1/2)H_2A_{2(o)} + B_{(o)} \overset{K_{AB}}{\rightleftharpoons} RE(NO_3)_2AB_{(o)} + H_{(a)}{}^{+} \quad (9)$$

$\log K_{AB}$ of Sm^{3+} and Y^{3+} can be calculated as 1.2 and 0.9, respectively.

It should be noted that there are differences between the results obtained from Fig. 2 and those obtained from Eq. (9). In Fig. 2, R reaches largest at the mole fraction of $X_{CA100} = 0.4$. Theoretically, the association of extractants should have a ratio of 2:3 (CA100:phen)

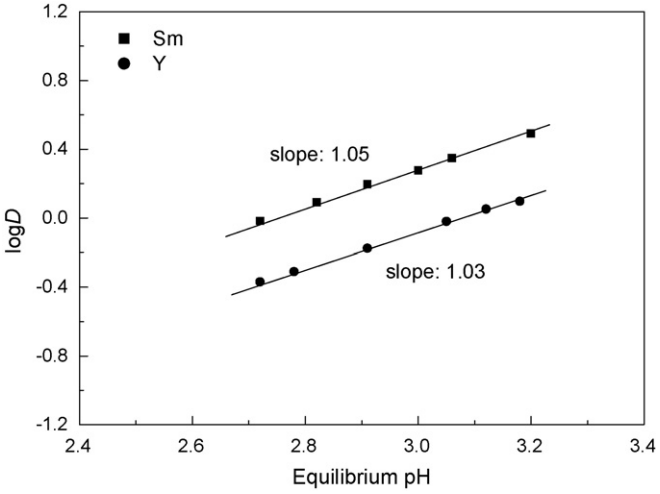

Fig. 3. Effect of pH on the extraction of Sm^{3+} and Y^{3+} with CA100 + phen. $[Sm^{3+}] = [Y^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, $\mu = 0.6$ mol L^{-1}, $C_{CA100} = 0.004$ mol L^{-1}, and $C_{phen} = 0.006$ mol L^{-1}.

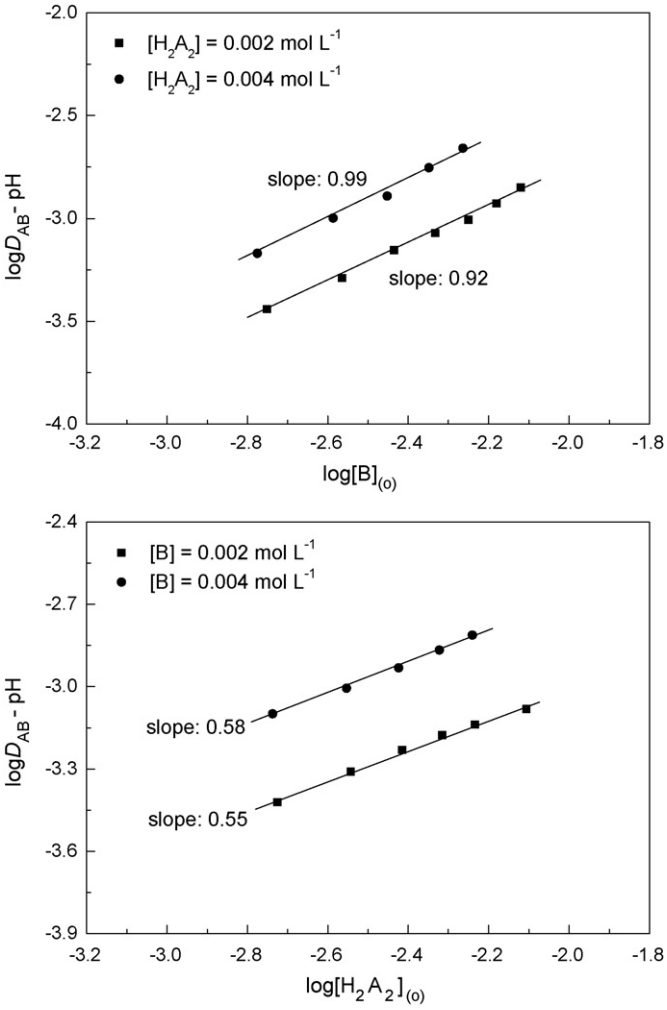

Fig. 4. Effect of extractant concentration on the extraction of Sm^{3+} with CA100 + phen. $[Sm^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH 3.0, and $\mu = 0.6$ mol L^{-1}.

in the extracted species. However, the synergistic extraction and the extraction with CA100 or phen alone exist simultaneously in the mixing system, the three reactions affect R values and determine the largest synergistic effects. Therefore, the stoichiometry is often not exactly in accordance with the mole fraction at which R reaches maximum. Similar results have also been reported in some previous papers [21,22].

3.3. Separation factors for REs with mixtures of CA100 and phen

The difference of synergistic effect for REs can be considered to separate them. Table 2 shows the separation factors ($\beta_{Ln/Y}$). It can be concluded that the selectivity between Ln^{3+} and Y^{3+} with CA100 + phen is higher than that with CA100 alone. Therefore, the mixtures of CA100 and phen can be used for the separation of Y^{3+} from Ln^{3+} at an appropriate ratio of the extractants.

Table 2
Separation factors of rare earths ($\beta_{Ln/Y}$) in CA100 and CA100 + phen systems.

Extractant	La/Y	Nd/Y	Sm/Y	Tb/Y	Yb/Y
CA100	1.7	1.3	1.2	1.0	0.9
CA100 + phen	0.5	1.8	2.5	1.3	1.5

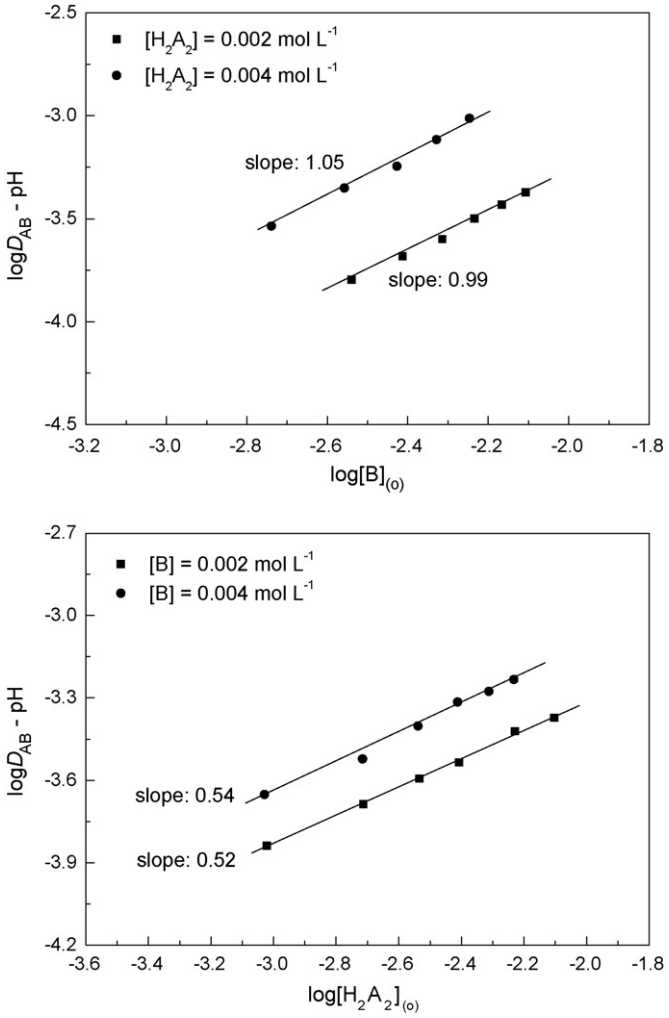

Fig. 5. Effect of extractant concentration on the extraction of Y^{3+} with CA100 + phen. $[Y^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH 3.0, and $\mu = 0.6$ mol L^{-1}.

3.4. Temperature dependency of the synergistic extraction

The effects of temperature on the extraction of Sm^{3+} and Y^{3+} with the mixtures of CA100 and phen have been studied at fixed aqueous acidity and concentrations of CA100 and phen. Fig. 6 shows the plots of log D versus [1000/T (K)], giving slopes of −0.20 (Sm^{3+}) and −0.59 (Y^{3+}), respectively. The change of enthalpy of the reaction, ΔH, can be determined according to the following equation:

$$\frac{\Delta \log D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \quad (10)$$

The change of Gibbs free energy, ΔG, and the change of entropy, ΔS of the system at 293 K can be obtained:

$$\Delta G = -RT \ln K \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (12)$$

Table 3
Thermodynamic parameters of Sm^{3+} and Y^{3+} extracted with CA100 + phen systems.[a].

RE	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Sm^{3+}	3.9	−6.6	35.9
Y^{3+}	11.4	−4.8	55.3

[a] ΔG and ΔS have been calculated at 293 K.

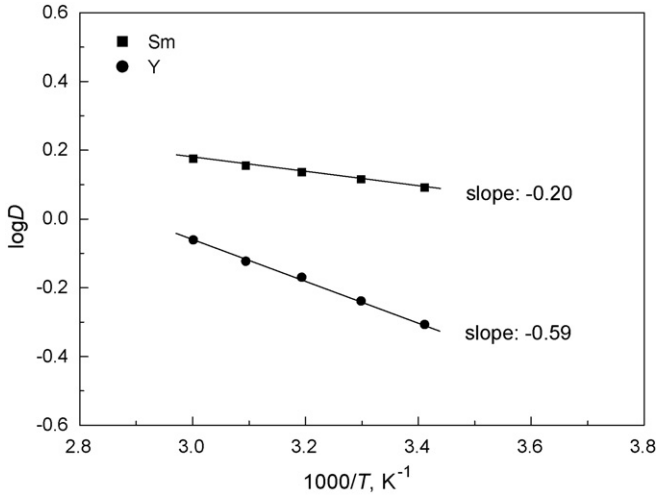

Fig. 6. Effect of experimental temperature on the extraction of Sm^{3+} and Y^{3+} with CA100 + phen. $[Sm^{3+}] = [Y^{3+}] = 1 \times 10^{-3}$ mol L^{-1}, pH 3.0, $\mu = 0.6$ mol L^{-1}, $C_{CA100} = 0.004$ mol L^{-1}, and $C_{phen} = 0.006$ mol L^{-1}.

ΔH, ΔG, and ΔS can be obtained as shown in Table 3. The signs of ΔH in CA100 + phen systems are positive, indicating that the extraction procedures of Sm^{3+} and Y^{3+} with the mixtures are endothermically driven. In addition, the signs of ΔS for Sm^{3+} and Y^{3+} are both positive, which is in accordance with the theory of increasing of entropy form the view of statistics.

4. Conclusions

Mixtures of CA100 and phen in benzene show evident synergistic effects when used for the extraction of rare earths (La, Nd, Sm, Tb, Yb, and Y) from nitrate medium. The stoichiometries of the extracted complexes for Sm and Y have been determined by graphical and numerical methods. The equilibrium constants and thermodynamic parameters have been investigated. The synergistic extractions of Sm and Y are both determined as endothermic processes. The mixtures of CA100 and phen have higher selectivities when applied to the separation of lanthanoids and yttrium.

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