

# Preparation of High Purity Rare Earth Metals of Samarium, Ytterbium and Thulium



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**Abstract:** High purity rare earth metals, including samarium, ytterbium and thulium, were prepared by vacuum reduction-distillation of each rare earth oxide with lanthanum metal. The results show that the rare earth metals of samarium and ytterbium with 4N-purity are obtained by direct vacuum reduction-distillation, and their purity is 99.99 wt% and 99.993 wt%, respectively, with respect to 75 impurities. There is a high concentration of reductant in thulium metal due to the higher reaction temperature and lower distillation velocity ratio of metallic thulium to lanthanum, so that the sublimation purification with lower temperature and high vacuum is needed. The purified thulium can reach a high purity of 99.995wt% with respect to 75 impurities. Therefore, the preparation of high purity reductant of lanthanum metal, especially of total amount control of metallic impurities, is the key step to obtain 99.99%-purity rare earth metallic samarium, ytterbium and thulium.

**Key words:** vacuum reduction-distillation; high purity rare earth metals; samarium; ytterbium; thulium

The highly volatile lanthanide metals, samarium, europium, ytterbium and thulium, are usually prepared by a vacuum reduction-distillation method, which is to reduce directly rare earth oxides with a non-volatile reductant such as lanthanum or cerium metal at high temperature. Generally speaking, the purity of reduction product can reach 99.5~99.9 wt%; it is well known that the purity of rare earth metals is closely related to the intrinsic property and the function of rare earth materials, so that the reduction product should be purified by vacuum distillation and/or sublimation to a high purity to meet the demands of materials technology development. Up to now, there are few researches concerning the preparation of volatile rare earth metals. Kazuyoshi<sup>[1,2]</sup> studied the fundamental on the production of rare earth metals (samarium, europium, ytterbium and thulium) by a direct reduction process, and found that the reactivity for reduction of each oxide was better in the order of europium oxide>yterbium oxide>samarium oxide> thulium oxide; Z. Hao<sup>[3]</sup> prepared the metallic samarium by reducing samarium oxide with rich-lanthanum

alloy, and the purity of reduction product is 99.78 wt% with respect to 10 impurities; W. Chen<sup>[4]</sup> prepared metallic europium by 2-step of distillation and ingot casting, and the concentration of oxygen is less than 300 µg/g; B. Wu<sup>[5]</sup> calculated the thermodynamic parameters of the reduction of metallic ytterbium by lanthanum or cerium, and prepared the metallic ytterbium with purity of 98.56wt% and 98.43wt%, respectively, by above two kinds of reductant with respect to 12 impurities. The thermodynamic behavior of RE(rare earth) impurities and non-RE impurities has been discussed, and some technical measures to improve purity degree of metallic ytterbium has been proposed<sup>[6]</sup>; G. Busch<sup>[7]</sup> purified europium with ultra high vacuum distillation in a simple quartz apparatus, and the total concentration of impurities (including gases) was found to 170 µg/g A. M. Ionov<sup>[8]</sup> compared the purification effects of samarium, europium, ytterbium and thulium by three methods: sublimation of solid metal, sublimation through porous tungsten filter and distillation through liquid lanthanum or cerium metal, and high purity rare earth metal with residual

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resistance ratio (RRR) of 300 were obtained, but concentration of impurities was not measured by chemical analysis, and the purity of metals has not been determined.

In the present study, europium metal is oxidized easily in the process of sampling and chemical analysis, so that others high purity volatile rare earth metals have been prepared.

## 1 Experiment

The first attempt with commercial metallic lanthanum was to reduce the samarium oxide, and a high concentration of Ca, Mg, Si, Fe and C impurities were found in the reduction product, because the purity of the commercial metallic lanthanum is about 99 wt%, and the above impurities are brought into the reduction product. Consequently, the key point in the preparation of high purity rare earth metals is to avoid the impurities introduced by starting materials, and the purification of the starting materials must be carried out firstly. During the whole preparation process, the operation environment must be kept clean through the whole preparation process.

The preparation of high purity samarium, ytterbium and thulium includes two steps, the first step is to prepare high purity reductant, lanthanum metal; the second step is to direct reduction-distillation rare earth oxide by lanthanum in vacuum atmosphere, and the subsequent vacuum distillation/sublimation purification. The schematic diagram of equipment is shown in Fig.1.

Gaseous impurities, including carbon, oxygen, hydrogen and nitrogen, were analyzed by interstitial gas analysis (IGA), and other impurities were analyzed by glow discharge mass spectrometry (GDMS).

## 2 Results and Discussion

### 2.1 Preparation of Lanthanum

Metallic lanthanum is prepared by metallothermic reduction of fluoride with calcium.  $\text{LaF}_3$  is obtained by the dry method, the anhydrous HF is passed over the  $\text{La}_2\text{O}_3$  at 650~700 °C for 16 h, and then the mixture of  $\text{LaF}_3$  and Ca are packed into the tungsten crucible, an excess of 10% of Ca more than

stoichiometric amount. The crucible is located in the vacuum induction furnace, and heated to 1400~1600 °C for about 2 h under the protection of argon gas, and poured into a tungsten mould. In the solidification process of the crude lanthanum metal, some inclusions will be entrapped, such as  $\text{LaF}_3$  and  $\text{CaF}_2$ , and excess reductant will be left in the matrix metal, but the above inclusions and impurity can volatilize easily, so that the poured metal is re-melted at 1400~1500 °C in the vacuum environment to remove above volatile inclusions and impurities.

The refined metallic lanthanum was sampled and analyzed, as seen in Table 1. The GDMS analytical results indicate that the amount of metallic impurities is 185  $\mu\text{g/g}$ , the concentration of impurities of Ca and F are both less than 5  $\mu\text{g/g}$ , but the crucible impurities, such as W and Ni, reach 79 and 58  $\mu\text{g/g}$ , respectively, and the amount of above two impurities is about 74% of the total metallic impurities in lanthanum metal, which are introduced in the procedure of fluoridation in nickel tube and reduction in tungsten crucible.

According to the Handbook<sup>[9]</sup>, the saturated vapor pressures of W and Ni are much lower than that of samarium, ytterbium and thulium, so that they will be removed in the vacuum reduction-distillation or subsequent distillation/sublimation process, and the rare earth metal will not be contaminated.

As stated above, lanthanum metal, obtained by vacuum melting, can satisfy the request of preparation of high purity rare earth metals.

### 2.2 Preparation of high purity samarium

To evaluate the contamination degree of reductant (lanthanum) to the reduction product (samarium), or the separation degree in the distillation purification, a dimensionless ratio of distillation velocity of metallic samarium to lanthanum, has been considered, as shown in Fig.2.

The dimensionless ratio is greater than  $1.2 \times 10^7$  at 1200 °C, and it is found that the distillation velocity ratio is decreased gradually with the temperature increasing, and this curve also confirms the research result of Kazuyoshi<sup>[11]</sup>, which is low temperature distillation is beneficial to obtain high purity rare earth metals. However, considering the melting point of reactants and products and the reaction rate, a proper reduction temperature should be chosen. In the process of high vacuum distillation purification, it is the best to distill or sublimate at low temperature, so the residual reductant

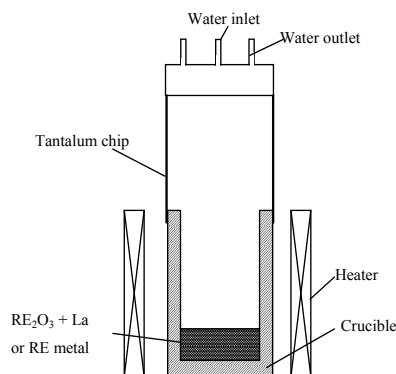


Fig.1 Schematic diagram of reduction-distillation and purification

Table 1 Analytical results of lanthanum metal ( $\mu\text{g/g}$ )

Sc	Y	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
<0.005	6.7	1.2	<0.5	0.39	<0.05	<0.05	2.3	1.6	<0.05
Ho	Er	Tm	Yb	Lu	Si	Ca	Mg	Fe	Mn
<0.05	<0.05	<0.05	<0.05	<0.05	3.8	5	<0.05	4.6	0.03
Al	Ti	Ni	Co	Cu	Pb	Zn	Sn	Cd	Ta
3.3	0.85	58	0.02	1.1	0.24	<0.05	<0.05	<0.05	<1
Zr	Pt	Nb	Cr	W	Mo	Na	F	S	P
0.16	<0.05	<0.05	<0.05	79	15	0.08	<5	1.7	0.005

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