

Solid-State Synthesis of Metastable Ytterbium (II) Oxide

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Abstract

Due to its electron configuration (Xe) 4 f¹⁴ 6 s², Ytterbium (Yb) could form divalent oxide, YbO. In this study, the solid-state synthesis of metastable YbO was investigated by the oxidation of Yb metal at normal pressure using two experimental conditions: 1) heat treatment of Yb metal under Ar gas atmosphere with metal carbonate as an oxygen source; and 2) heat treatment of Yb metal under the continuous gas flow condition using various gas atmospheres. Products were identified using the powder X-ray diffraction and scanning electron microscope. It was found that almost single phase YbO was obtained in the experimental condition 1) using the molar ratio of $CaCO_3/Yb = 0.4$. Thermodynamic calculations suggested that the YbO formation be controlled not by thermodynamics but by kinetics, and further that the evaporation of Yb metal in the BN crucible played a key role for the formation of the meta-stable YbO.

Keywords

Metastable Ytterbium (II) Oxide, Lanthanide, Solid-State Synthesis

1. Introduction

It is well known that lanthanide ions have a common stable valence, 3+. Since the ionization energies to change from Ln^{2+} to Ln^{3+} is larger only in Europium (Eu) with the electron configuration (Xe) 4 f⁷ 6 s² and Ytterbium (Yb) with the electron configuration (Xe) 4f¹⁴ 6s² than in the other lanthanides, divalent Eu and Yb could be stable [1]. In fact, it has been known that Eu readily reacts with water or dilute acids to form divalent compounds [2] [3]. Europium oxide (EuO) and Europium sulfide (EuS) are commercially available, and have been used as a fluorescent material [4]. However, there has been much less reports for synthesizing divalent ytterbium compounds. It was suggested that YbO could exist as a metastable phase because the standard Gibbs free energy change ($\triangle G^0$) in the reaction (1) was very close to 0 by the theoretical calculations as shown in **Figure 1** [5]:

$$Ln + Ln_2O_3 \rightarrow 3Ln^{2+}O^{2-} \tag{1}$$

YbO was synthesized under very high pressure at 50 kbar through the reaction (1). It was reported that the Gibbs free energy change for the reaction (1) was estimated from +8 to +13 kcal/mol in this condition [5] [6]. The formation of YbO was also confirmed through the oxidation of Yb metals dissolved in liquid ammonia [7]. However, the use of very high pressure or ultra-low temperature seems to be unrealistic when considering the industrial production. There has been no report on the synthesis of YbO under the normal pressure until now.

In the course of oxidation from Yb metal to Yb_2O_3 , it would be highly possible that the metastable YbO phase be formed. In this work, the solid-state synthesis of YbO has been investigated by the oxidation of Yb metal under the normal pressure using two methods: 1) heat treatment of Yb metal under Ar gas atmosphere with metal carbonate as an oxygen source; and 2) heat treatment of Yb metal under the continuous gas flow condition using various gas atmospheres, Ar-O₂, Ar-CO and Ar-CO₂ in the tube furnace changing the ratio of mixed gas, temperature and retention time. A mechanism for the formation of YbO under various gas atmospheres was discussed based on the identification results obtained by using the X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).



 $Ln^{2+}O^{2-}$ [5].

2. Materials and Methods

2.1. Experimental Condition 1) Synthesis of YbO Using Carbonate as an Oxygen Source

Ytterbium metal powder (-20 mesh, 99.9%, RARE METALLIC Co., Ltd., Tokyo, Japan) was used as a starting material. Paraffin was removed from Yb metal powder by filtering, and washed off using hexane. 1.5 g of Yb metal powder was put into BN crucible (30 mm $\Phi \times$ 30 mmH, Denka CO., Ltd., Tokyo, Japan). An equi-molar of MCO₃ (M = Ca or Sr) was put into another BN crucible as an oxygen source expecting that the reactions (2) and (3) would proceed:

$$MCO_3 \to MO + CO_2 \tag{2}$$

$$Yb + CO_2 \rightarrow YbO + CO \tag{3}$$

 MCO_3 were chosen considering the melting point of Yb, 824°C, and the dissociation temperature of alkaline-earth metal carbonate as shown in Table 1. A BN crucible with a lid containing Yb metal powder and another one without a lid containing MCO_3 were placed together in a graphite susceptor as shown in Figure 2.

Table 1. Temperatures at which the CO_2 dissociation pressures of alkali carbonates MCO_3 reaches 1 atm [8].

MCO ₃	Temperature (°C)	
M = Mg	~600	
M = Ca	898	
M = Sr	1155	
M = Ba	1421	



Figure 2. Schematics of the experimental condition 1): two BN crucibles containing Yb metal powder and carbonate are together placed in a graphite susceptor.

The samples heat-treated using an atmospheric high-temperature furnace (FVPHP-R-3 type, Fuji Dempa Kogyo Co., Ltd., Osaka, Japan) which consisted of graphite heating elements and graphite thermal insulating materials. Heat-treatment was conducted at 750°C for 4 or 6 hrs under 0.2 MPa Ar atmosphere. The heating and cooling rates were both 10°C/min.

In the case of MCO₃ (M = Ca), the Yb metal to MCO₃ ratio was changed such as Yb:MCO₃ = 1:2, 1:1, 4:3, 2:1, 5:2 and 10:3, and heat-treated at 750°C for 6 hrs under 0.2 MPa Ar atmosphere. The phase analysis and microstructural observation of the products were investigated using the XRD (XRD-7000L, Shimadzu Corp.) and the field emission SEM (FE-SEM: JSM-7100F/TTL, JEOL Ltd.) with an energy dispersive x-ray spectrometry (EDX) equipment, respectively.

2.2. Experimental Condition 2) Synthesis of YbO under the Continuous Gas Flow Condition

1.5 g of Yb metal powder was put into a BN crucible without a lid, which was put into a Mullite ceramic tube ($50 \times \varphi 42 \times 500 \text{ mm}$) in the tube furnace (TMF-500 type, AS ONE Corporation, Osaka, Japan) as shown in **Figure 3**. Carbon felt was inserted into the tube in the front of a crucible. After evacuation, Ar was flowed for 1 hr at a flow rate of 2 ml/min, and then, mixed gas was started to flow at each mixing ratio using the same flow rate. Under the experimental conditions used in this work, it was expected that O₂ gas was almost completely converted to CO in the furnace. **Table 2** summarizes the heat-treatment conditions examined in this work. Heating rate was 10° C/min and after heat-treatment, the furnace was naturally cooled down. For obtaining the Ar-H₂O mixed gas, Ar gas was passed through a bottle of water at a constant temperature. The phase analysis and microstructural observation of the products were investigated using the XRD and FE-SEM with EDX, respectively.

3. Results and Discussion

3.1. Synthesis of YbO Using Carbonate as an Oxygen Source

Figure 4 shows the XRD patterns of products heat-treated at 750°C for 4 and 6 hrs with $CaCO_3$, (a) and (b), or $SrCO_3$, (c) and (d). The YbO phase is confirmed in **Figure 4(a)** and **Figure 4(b)**. In particular, No Yb phase exist, and only two phases, the Yb₂O₃ and the YbO phases, are observed in (b). The YbO phase is also observed in **Figure 4(c)** and **Figure 4(d)**, however, their peak intensities are much weaker and the peak intensities of the Yb phase are much stronger than those in **Figure 4(a)** and **Figure 4(b)**. Since evolved CO_2 gas immediately reacts with the surrounding graphite to yield CO gas, the extent of Yb metal oxidation would depend on the oxygen partial pressure determined by the CO and CO_2 partial pressures dissociated from metal carbonate. From these results, it would be concluded that the amount of CO_2 dissociated from $CaCO_3$ at 750°C be suitable for the synthesis of YbO. This point will be discussed further in the later section.



Figure 3. Schematics of the experimental condition 2): heat-treatment of Yb metal powder under the continuous gas flow in a tube furnace using different gas mixtures. Note that CO gas was generated by passing oxygen gas through the carbon felt.

Table 2. XRD result of the products that were obtained by the heat-treatment of Yb metal under the flowing gas condition using various gas mixtures.

Atmosphere	Flow rate* (mL/min)	Temp. (°C)	Time (h) –	XRD results		
				Yb	YbO	Yb ₂ O ₃
Only Ar	0	750	6	v s	w	S
$Ar + O_2$	20	750	6	v s	v w	S
	20	750	6	w	m	v s
		750	4	s	v w	v s
		650	6	m	v w	v s
$Ar + CO_2$	2	650	6	m	v w	v s
		650	1	v s	v w	w
		850	1	v s	v w	w
			1	s	v w	v s
		600	3	m	v w	v s
		650	1	w	v w	v s
			3	w	v w	v s
			6	w	v w	v s
		700	1	s	v w	v s
			3	v w	v w	v s
$Ar + CO^{**}$	2	750	1	v s	v w	s
AI + CO 2			3	m	v s	v s
			6	v w	s	v s
			8	w	w	v s
			10	ND	w	v s
			0	m	v w	v s
		800	1	v w	S	v s
		300	3	v w	v w	v s
			6	ND	ND	v s

vs: very strong; s: strong; m: middle; w: weak; vw: very weak; ND: Not Detected; *Flow rates shown here are those of O_2 or CO_2 , and that of Ar was fixed at 2.0 L/min; **CO was not used in this experiment; O_2 and carbon felt were used to produce CO.



Figure 4. XRD patterns of products heat-treated with metal carbonate at 750 °C for 4 or 6 hrs: (a) $CaCO_3$, 4 hrs; (b) $CaCO_3$, 6 hrs; (c) $SrCO_3$, 4 hrs; (d) $SrCO_3$, 6 hrs.

Figure 5 shows the SEM micrographs of Yb metal powder heat-treated at 750°C for 4 hours with CaCO₃. A left micrograph taken at low magnification demonstrate the existence of large particles with about 100 m diameter and numerous spherical particles with a few micron diameter. A right micrograph taken at high magnification reveals that some of the fine spherical particles have micro cracks. It is observed that the large particles keep the shape of the raw Yb metal powder, and thus, it would be conclude that fine spherical particles would be not Yb metal but the Yb₂O₃ or YbO phase.

The XRD results of heat-treated Yb metal by changing the CaCO₃/Yb ratio with or without a BN lid are summarized in **Table 3**. No Yb phase exists, and the YbO and Yb₂O₃ phases are confirmed in all products. The peak intensity of the YbO phase increases and that of the Yb₂O₃ phase decreases with decreasing the CaCO₃/Yb ratio. The peak intensity of the YbO phase was the strongest in the product obtained by the CaCO₃/YbO ratio = 0.4, which was close to the YbO single phase. It is especially noteworthy that the peak intensity of the Yb₂O₃ phase was much stronger in the case without a lid on the BN crucible than that with a lid. This point will be also discussed further in the later section.

Unfortunately, it was found that the repreducibility of the products was very low, which might be due to the difference of the atmosphere inside the graphite and/or BN crucibles, and also the usage history of BN crucible such as the porosity change. Thus, the heat treatment under controlled atmosphere in the tube furnace was tried in the next section.

3.2. Synthesis of YbO under the Continuous Gas Flow Condition

Table 2 summarizes the XRD result of products heat-treated under continuous



Figure 5. SEM photographs of the sample of Yb was heat-treated at 750°C with $CaCO_3$ at 750°C for 4 hours: (a) 250× and (b) 5000× magnifications.

CaCO ₃ /Yb	With/without a lid	Yb	YbO	Yb ₂ O ₃
2		ND	w	v s
1		ND	w	V S
0.75	TA7'-1 1' 1	ND	s	V S
0.5	with a lid	ND	v s	w
0.4		ND	v s	v w
0.3		ND	v s	v s
0.4	Without a lid	ND	v s	s

Table 3. XRD results of the products that were obtained by the heat-treatment of Yb metal by changing the $CaCO_3/Yb$ ratio.

v s: very strong; s: strong; m: middle; w: weak; v w: very weak; ND: Not detected.

gas flow in a tube furnace. In the case of only Ar gas and Ar-O₂ mixed gas, it was confirmed that the Yb and Yb₂O₃ phases were the primary and the second phas-

es, respectively. Thus, it is suggested that these atmospheres are not suitable for the synthesis of YbO. When Ar-CO₂ mixed gas was used, the Yb₂O₃ and Yb phases were the primary and second phases, respectively. However the diffraction peak of YbO was observed to be a little stronger than those treated in only Ar and Ar-O₂ mixed gas. Under the Ar-CO atmosphere, the primary phase was confirmed to be Yb₂O₃, however, the second phase was the YbO phase in some conditions. Then, it might be possible to find the condition that YbO becomes the primary phase by adjusting the holding temperature and time under the Ar-CO atmosphere. As the retention time is prolonged, the reaction from Yb to YbO proceeds, at the same time, the reaction from YbO to Yb₂O₃ also progresses. The peak intensity of the YbO phase was the strongest when heat-treated at 750°C for 6 hrs among the current atmosphere, however those of the Yb₂O₃ phase was very strong.

Figure 6 shows SEM photographs of Yb metal powder heat-treated at 650°C, 750°C and 800°C for 6 hrs under the Ar-CO atmosphere. The SEM photograph of the raw Yb metal powder is also shown in this figure for comparison. As described





Figure 6. SEM photographs of Yb metal powder heat-treated at (a) 650°C; (b) 750°C and (c) 800°C for 6 hrs under Ar-CO atmosphere. That of the raw Yb metal powder is also shown in (d).

in 3.1, fine spherical particles were observed also in this case, and it was found that the amount of fine spherical particles increased with increasing temperature. It is assumed that the spherical particles are YbO or Yb_2O_3 , because large particles keeping the shape of the Yb metal powder are no longer visible when heat-treated at 800°C for 6 hrs. Probably, these spherical particles would be formed by the reaction of vaporized Yb with the atmosphere, and deposited on the surface of the Yb metal powder.

3.3. Formation Mechanism of Metastable YbO

3.3.1. Thermodynamics

The formation mechanism of YbO in this study was discussed based on the thermodynamic calculations as follows.

In the experimental condition 1), it is expected that the reaction (4) proceeded to the left, and CO_2 was generated while the sample was heat-treated in a graphite susceptor:

$$CaO + CO_2 \rightleftharpoons CaCO_3$$
 (4)

The standard Gibbs free energy changes of reactions (4) is given as follows:

$$\Delta G_4 = -168.410 + 143.9 \cdot T \tag{4'}$$

Since the generated CO_2 immediately reacts with graphite, which is the material of the suceptor and the high-temperature furnace with graphite heating elements, the reaction (5) proceeds to the right, and it is expected that the oxygen partial pressure determined by the CO and CO_2 partial pressure would control the extent of Yb metal oxidation.

$$C + CO_2 \rightleftharpoons 2CO$$
 (5)

$$\Delta G_5 = 170.700 - 174.46 \cdot T \tag{5'}$$

Using the thermodynamic data of the Equations (6) and (7), the standard Gibbs free energy changes of reactions (5), ΔG_5 , is obtained as shown above:

$$C + O_2 \leftrightarrows CO_2 \tag{6}$$

$$\Delta G_6 = -394.100 - 0.84 \cdot T \tag{6'}$$

$$2CO + O_2 = 2CO_2 \tag{7}$$

$$\Delta G_7 = -564.800 + 173.62 \cdot T \tag{7'}$$

The equilibrium constant of the reaction (5) at temperature T(K), K_T , is determined using ΔG_5 as follows:

$$K = \frac{p_{CO}^2}{a_c \cdot p_{CO_2}}$$
$$\Delta G_5 = -RT \ln K$$
$$\therefore \frac{p_{CO}^2}{p_{CO_2}} = e^{-\frac{\Delta G_5}{RT}} = K_T$$
(8)

From the reaction (4), the dissociation pressure of $CaCO_3$ at temperature T(K)

is given as follows:

$$K = \frac{a_{CaCO_3}}{a_{CaO} \cdot p_{CO_2}} = p_{O_2}^{-1}$$

$$K = e^{-\frac{\Delta G_4}{RT}}$$

$$(\because \Delta G_4 = -RT \ln K)$$

$$\therefore p_{CO_2} = e^{-\frac{\Delta G_4}{RT}}$$
(9)

In the reaction (5), the CO₂ partial pressure, p_{CO_2} , before equilibrium is given by the Equation (9). Setting the CO partial pressure, p_{CO} , at equilibrium as *x*, the equilibrium constant K_T is expressed as follows:

$$\frac{x^2}{p_{\rm CO_2} - \frac{x}{2}} = K_T \tag{10}$$

when Equation (10) is solved for x, Equations (11) and (12) are given for $p_{\rm CO}$ and $p'_{\rm CO_2}$ at equilibrium as follows:

$$p_{\rm CO} = -\frac{K_T}{4} + \sqrt{\frac{K_T^2}{16} + K_T \cdot p_{\rm CO_2}}$$
(11)

$$p'_{\rm CO_2} = p_{\rm CO_2} - \frac{1}{2} p_{\rm CO} \tag{12}$$

The equilibrium constant, *K*, of the reaction (7) would be expressed in order to determine the oxygen partial pressure, in this mechanism as follows:

$$K = \frac{p'_{\rm CO_2}}{p^2_{\rm CO} \cdot p_{\rm O_2}} = e^{-\frac{\Delta G_7}{RT}}$$
(13)

Substituting the Equations (11) and (12) into the Equation (13), p_{0_2} would be expressed as follows:

$$p_{O_2} = \left(\frac{p'_{CO_2}}{p_{CO}}\right)^2 \cdot e^{\frac{\Delta G_7}{RT}}$$
(14)

It is possible to calculate the oxygen partial pressure during the heat treatment using CaCO₃ as an oxygen source through this series of calculations, and **Figure** 7 shows the oxygen partial pressure as a function of temperature. It is suggested that the oxygen partial pressure in experiment 2) would be much larger than that in experiment 1) by this calculation result probably due to the flowing gas condition. Furthermore, it is clear that the oxygen partial pressure of Yb₂O₃ formation calculated from the following thermodynamic data [9] is much lower than the p_{CO2} obtained by the Equation (14) as shown in **Figure 7**, which would suggest that the formation of YbO in the experimental condition 1) be controlled not by thermodynamics but by kinetics:

$$2Yb + 3/2O_2 \rightleftharpoons Yb_2O_3 \tag{15}$$

$$\Delta G_8 = -1817.859 + 0.277977 \cdot T \tag{15'}$$



Figure 7. Oxygen partial pressure as a function of temperature (broken and solid lines express Equations (14) and (15), respectively).

3.3.2. Mechanisms of YbO Formation

From the results obtained in the experimental conditions 1) and 2), two mechanisms regarding the generation of fine YbO or Yb₂O₃ particles outside the Yb metal paticles could be considered. The generation of fine YbO or Yb₂O₃ particles outside the Yb metal particles would be attributed to the characteristics of Yb metal, which has remarkably high vapor pressure, about 1 kPa at 774°C, near its melting point 824°C [10]. Thus, the formation of fine oxide particles would be attributed to the vapor phase reaction. The generation and deposition of fine spherical particles shown in Figure 5 and Figure 6 would be the evidence of vapor phase reaction. The second mechanism that the oxide particles generated from the inside of the metal particles would be the solid-vapor reaction mechanism like the general metal oxidation mechanism shown in Figure 8 [11]. It is generally known that the oxidation of metal occurs on the metal surface, then cracks are generated by a density difference between oxide and metal as oxidation progressing from the surface to the bulk. Figure 9 shows the cross section of a particle obtained in the experimental condition 2) under the Ar-CO atmosphere. Obviously some darker parts different from the surrounding are observed, at which fine cracks were confirmed at high magnification. As shown in Table 4, there is a considerably large density difference between Yb, YbO and Yb₂O₃, which would be the cause of cracks.

SEM photographs of the sample composed of almost YbO single phase are shown in Figures 10(a)-(c). Figure 10(a) taken at low magnification shows very porous aggregates composed of fine particles, which would be significantly different from the large particles with about 100 m size keeping the raw Yb metal powder observed in Figure 5(a) and Figure 6(a). Figure 10(b) taken at high magnification demonstrates the existence of fine spherical particles with a few micron size, which seems to be similar to those observed in Figure 5(b) and

Cracks in oxide

Figure 8. Schematics of the typical metal oxidation on the metal surface [11].



Figure 9. SEM photographs showing the cross section of a particle obtained in the experimental condition 2) under the Ar-CO atmosphere: (a) $500 \times$ and (b) $10,000 \times$ magnifications.

Table 4. Densities of Yb, YbO an	$d Yb_2O_3$.
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Substance	Density/g·cm ⁻³		
Yb	7.01		
УЪО	10.84		
Yb ₂ O ₃	9.22		

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Figure 10. SEM photographs of the sample obtained by the $CaCO_3/Yb = 0.4$ in experimental condition 1): (a) $500\times$; (b) $1500\times$; (c) $5000\times$ magnifications.

Figure 6(b). However, close observation shown in **Figure 10(c)** reveals the shape difference between them; fine spherical shapes in **Figure 5(b)** and **Figure 6(c)**, and rather facetted polycrystalline shapes in **Figure 10(c)**, suggesting that the formation mechanisms are different from each other. **Figure 11** shows the XRD pattern of the sample composed of almost YbO single phase obtained by the CaCO₃/Yb = 0.4 in experimental condition 1). Since it was found that the phase content was vastly different between two products which was obtained by the same heat treatment at 750°C for 6 hrs in BN crucible under 0.5 MPa Ar



Figure 11. XRD pattern of the sample composed of almost YbO single phase obtained by the $CaCO_3/Yb = 0.4$ in experimental condition 1).

atmosphere using the $CaCO_3$ /Yb ratio = 0.4 but with and without the BN lid, it is considered that the BN lid plays the key role for the single phase YbO formation. As described in 3-1), CO₂ gas generated from CaCO₃ reacts with graphite inside the susceptor as shown in Equation (5), in which a pseudo-equilibrium state would be achieved to give an oxygen partial pressure close to the value calculated by Equation (14). Without a BN lid, the Yb₂O₃ phase would be formed by the direct reaction between the Yb metal surface and oxygen with the partial pressure much larger than that for Yb₂O₃ formation resulting in the formation of Yb₂O₃ layer on the Yb metal surface that would suppress further direct oxidation. Because the density difference between the Yb metal and Yb₂O₃, cracks would be formed on the surface, and Yb metal vapor would erupt from the surface to form the spherical particles by the vapor reaction. In contrast, with a BN lid, a pseudo-equilibrium state would be achieved inside the BN crucible, in which the Yb metal vapor pressure would be significantly high. The Yb metal vapor erupts form the crucible, and simultaneously oxygen gas intrude into the crucible, across the porous BN wall, at which the reaction (15) would proceed to decrease the oxygen partial pressure low enough to form the single phase YbO on the Yb metal surface. The very porous structure and rather facetted polycrystalline particle morphology shown in Figures 10(a)-(c) would be the evidence of the Yb vaporization and the formation of YbO on the Yb metal surface. The fact that the single phase YbO was formed less than the stoichiometry at $CaCO_3/Yb = 0.4$ and the yield of YbO was about 50%, and the fact that no Yb metal phase was confirmed by XRD, both evidently support the Yb vaporization in the case with a BN lid.

Since two mechanisms for YbO formation, the vapor phase reaction and the solid-vapor reaction, have been proposed based on the results obtained in this study, the distribution of Yb, YbO and Yb_2O_3 on the surface or inside of the Yb metal particles remains unknown, since the FE-SEM with EDX was not able to detect the difference of these phases.

4. Conclusion

Two methods, static and flowing gas conditions, were studied for synthesizing

the metastable YbO under normal pressure using Yb metal as a starting material. When CaCO₃ was used as an oxygen source, almost single phase YbO was successfully obtained at 750°C for 6 hrs in BN crucible with a BN lid under 0.2 MPa Ar atmosphere using the CaCO₃/Yb ratio = 0.4. The flowing gas condition using Ar-CO gas mixture gave the highest content of YbO among the atmospheres examined in this study, however the Yb metal and Yb₂O₃ were always co-existed. Thermodynamic calculations suggested that the YbO formation be controlled not by thermodynamic but by kinetics, and further that the use of a BN lid would play a key role achieving the pseudo-equilibrium state inside the crucible to give extremely low oxygen partial pressure.

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