

# 価数揺動状態がある希土類の硫化物合成とその応用

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# Synthesis of Rare-Earth Sulfides (RE=Yb, Eu, and Sm) with Valence-Fluctuated Characters and Their Applications (価数揺動状態がある希土類の硫化物合成とそ の応用)

## A Dissertation

Submitted to Muroran Institute of Technology Division of Science for Composite Functions In Partial Fulfillment of the Requirements For the Degree of Doctor of Engineering

By

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## **Certificate of Approval**

This dissertation entitled:

Synthesis of Rare-Earth Sulfides (RE=Yb, Eu, and Sm) with

Valence-Fluctuated Characters and Their Applications

(価数揺動状態がある希土類の硫化物合成とその応用)

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The Final copy of this dissertation has been examined by the signatories, and we find that both the content and form meet acceptable presentation standers of scholarly work in the above mentioned discipline.

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#### Abstract

In some rare earth compounds, valences of rare earth elements take non-integer values, because valence values of rare earth elements fluctuate spatially and temporally. The fluctuated valences depend strongly on the synthesis temperature. In this study, Yb, Eu, Sm based sulfides with valence-fluctuation characters were to study the synthesis and stability and expected to discover new applications.

Ytterbium sulfides were prepared from  $CS_2$  sulfurization of  $Yb_2O_3$  and then heat treatments. Ytterbium sulfides ( $Yb_3S_4$  and YbS) are expected to be employed as high temperature n-type thermoelectric materials due to their large Seebeck coefficient.

The influences of particle size and specific surface area of Yb<sub>2</sub>O<sub>3</sub> powders, sulfurization temperature and time and CS<sub>2</sub> gas flow rate on preparation of ytterbium sesquisulfide (Yb<sub>2</sub>S<sub>3</sub>) were researched. Small particle size ( $< 1 \mu$ m) and large specific surface area ( $> 2 m^2/g$ ) of Yb<sub>2</sub>O<sub>3</sub> are necessary for fabrication of pure Yb<sub>2</sub>S<sub>3</sub>. Single orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> were synthesized by the sulfurization of fine Yb<sub>2</sub>O<sub>3</sub> powders at 700 ~ 800 °C and 1000~1050°C with CS<sub>2</sub> gas flow rate of 1.67 mL/s, respectively. Orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> transformed to hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> with increase of temperature. The heat treatments of Yb<sub>2</sub>S<sub>3</sub> were investigated. Upon heat treatment at 1000 °C for 3 hr in Ar/CS<sub>2</sub> atmosphere, orthorhombic Yb<sub>2</sub>S<sub>3</sub> phase underwent phase transition to hexagonal Yb<sub>2</sub>S<sub>3</sub> phase. Moreover, orthorhombic Yb<sub>3</sub>S<sub>4</sub> was main phase after heat treatment at 1000 °C for 3 hr, or at 1200 °C for 1 hr, under vacuum (~1.2×10<sup>-3</sup> Pa). Single-phase YbS with a homogeneity range of YbS<sub>1.11-1.15</sub> could be synthesized by treatment at 1500 °C for 3 hr.

Secondly, europium sulfides were synthesized by  $CS_2$  sulfurization of  $Eu_2O_3$ . EuS is a ferromagnetic semiconductor with NaCl type crystal structure. As this temperature is in the proximity of the boiling point of hydrogen, EuS is a potential magnetic refrigeration material.

The effects of  $Eu_2O_3$  character and sulfurization conditions on the preparation of europium sulfides were researched. Single-phase  $Eu_3S_4$  and EuS can be obtained by  $CS_2$  gas sulfurization of spherical  $Eu_2O_3$  with larger specific surface area and small grain size at 500 °C for longer than 0.5 hr and 800 °C for 8 hr, respectively. Moreover, EuS can be fabricated from self-prepared needle Eu<sub>2</sub>O<sub>3</sub> at 750 °C for 8 hr. The higher sulfurization temperature and shorter sulfurization time accelerated the formation of high purity EuS. Specific surface area of synthetics lessened with the rising of sulfurization temperature and time. Synthetic pure Eu<sub>3</sub>S<sub>4</sub> were treated under rich-sulfur atmosphere, inert atmosphere and vacuum, respectively. Single EuS phase was obtained at 973 K under rich-sulfur atmosphere or at 1073 K under inert atmosphere. The stability of Eu<sub>3</sub>S<sub>4</sub> during annealing is weaker than all above mentioned conditions and the transformation finished at 873 K under vacuum of 1.2 \*10<sup>-5</sup> Pa. The transformation of Eu<sub>3</sub>S<sub>4</sub> to EuS was attributed to stability of Eu<sup>2+</sup> at high temperature. The synthetic EuS powders were sintered under a uniaxial pressure of 50 MPa in vacuum. The large reversible magnetocaloric effect of polycrystalline EuS was observed, which underwent second-order ferromagnetic to paramagnetic transition at 16.8 K. The maximum of magnetic entropy change is as large as 6.32 J/mol/K and the adiabatic temperature change is 9.1 K under a vary magnetic field change of 5 T. The entropy value for polycrystalline EuS was revised by the combination of the magnetization and heat capacity data. The relative cooling power for polycrystalline EuS reached 69.26 and 125.39 J/mol for  $\Delta H = 3$  T and 5 T, respectively.

Finally, non-stoichiometric samarium monosulfide (SmS<sub>x</sub>, 0.55 < x < 1.2) was synthesized from Sm<sub>2</sub>S<sub>3</sub> and SmH<sub>3</sub> at 1273 K for 3 hr under vacuum. Until now, polycrystalline SmS prepared from the direct reaction between samarium and sulfur, has a thermoelectric figure of merit ZT ~0.9 with the optimal composition SmS<sub>0.96</sub>. The influence of reaction ratio of Sm<sub>2</sub>S<sub>3</sub> to SmH<sub>3</sub> on the fabrication of SmS was investigated.

The fabrication of SmS required the mole ratio of  $Sm_2S_3$  to  $SmH_3$  above 1. Lattice parameter of synthetic SmS increases firstly and then decreases to saturate following with the addition of  $SmH_3$  content. SmS compact was sintered at 1373 K by spark plasma sintering. Density of synthetic SmS is about 99% of theory density. Seebeck coefficient of n-type semiconductor  $SmS_x$  decreases as temperature rises. The absolute value is distributed between 170-280  $\mu$ V·K<sup>-1</sup>. The electrical conductivity of  $SmS_x$  (0.86<x<1.07) decreases with temperature increasing and shows similar temperature dependence. The surplus Sm which randomly distributed in the  $SmS_x$ (0.55<x<0.75) matrix, leads to a remarked reduces of electrical resistivity. The optimized power factor for SmS\_{0.6} and SmS\_{0.75} can reach 1500  $\mu W \cdot K^{\text{-2}} \cdot m^{\text{-1}}$  at 600 K.

#### 概要

価数揺動状態とは、価数が時間的に揺らぐことによって整数値から離れた 中途半端な値をとる場合のことである。価数揺動の特徴の一つに、価数が強く 温度依存することがある。本研究では、価数揺動状態がある Sm, Eu, Yb につい て、その用途に見合う単相の硫化物を合成することを目的とする。

最初に、Yb<sub>2</sub>O<sub>3</sub>の CS<sub>2</sub>ガス硫化と熱処理によるイッテルビウム硫化物を合成した。斜方晶 Yb<sub>3</sub>S<sub>4</sub>は p 型熱電材料、立方晶 YbS も 773 K 付近においてゼーベック係数が 1000µV/K に達した後、1023~1173 K 付近から高温では n 型になる熱電材料として期待されている。

硫化実験の結果、粒径が細かく、比表面積が大きな Yb<sub>2</sub>O<sub>3</sub> の場合、973~1073 K の低温の硫化では  $\eta$ -Yb<sub>2</sub>S<sub>3</sub>、1273~1373 K の高温の硫化では  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> 単相が生成した。これに対してさらに大きな比表面積の Yb<sub>2</sub>O<sub>3</sub> の場合、873K の硫化でも  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> 単相の生成が確認された。また、 $\eta$ -Yb<sub>2</sub>S<sub>3</sub> を真空中で熱処理すると Yb<sub>3</sub>S<sub>4</sub> が生成し、とくに長時間または高温で熱処理すると YbS を得ることができた。

次に、Eu<sub>2</sub>O<sub>3</sub>の CS<sub>2</sub> ガス硫化によりユーロピウム硫化物を合成した。EuS は NaCl 型結晶構造を有する強磁性半導体であり、磁気相転移温度が水素液化 温度(20 K)の近くにあるため、水素液化磁気冷凍の液化段に利用できる磁気 冷凍材料の候補材料である。

Eu<sub>2</sub>O<sub>3</sub>には細粒と粗粒を用意し、細粒の場合、硫化時間にかかわらず 773 K の硫化では Eu<sub>3</sub>S<sub>4</sub>単相、1073K の硫化では EuS 単相が生成した。EuS の生成は、 Eu<sub>2</sub>O<sub>3</sub>から EuS<sub>2</sub>を経て Eu<sub>3</sub>S<sub>4</sub>を生成し、次いで一部 Eu<sub>2</sub>O<sub>2</sub>S を生成しながら EuS を生成するものと推定した。一方、細粒の場合、硫化条件にかかわらず Eu<sub>3</sub>S<sub>4</sub> は生成せず、硫化時間が 1.8 ks と 28.8 ks の場合、低温で生成した Eu<sub>2</sub>O<sub>2</sub>S はそ れぞれ 1273 K と 1073 K より高温で消滅し、EuS 単相となった。すなわち、Eu<sub>2</sub>O<sub>3</sub> から Eu<sub>2</sub>O<sub>2</sub>S を経て EuS を生成することが確認された。

また、EuS 焼結体の磁気ゼロ及び磁場中(5T)の比熱を測定したところ、 磁気ゼロの場合は16.5 K に磁気転移に伴う大きなピーク、一方、磁場中は、ピ ークが磁場により広がりながら高温にシフトするという強磁性-常磁性状態 を二次相転移する常磁性体の典型的な変化を示した。また、MPMS を用いた磁 化測定から求めた単位体積当たりの磁気エントロピー変化の温度依存性から、 16.8 K 付近に山型のピークが確認され、単結晶で見られた磁気エントロピー変 化の値と一致した。すなわち、EuS 焼結体が単結晶と同等の磁気熱量効果を有 することが明らかになった。

最後に、Sm<sub>2</sub>S<sub>3</sub> 粉末と SmH<sub>3</sub> 粉末の反応焼結法により非化学量論組成の SmS<sub>x</sub>, (0.55<x<1.2)焼結体を作製した。これまで、Sm 金属と硫黄の直接反応 により SmS<sub>0.96</sub>が合成され、1000 K において性能指数(Z)が 0.9×10<sup>-3</sup> K<sup>-1</sup>に達 することが報告されている。最初に、BN 坩堝中で所定の配合比の Sm<sub>2</sub>S<sub>3</sub> と SmH<sub>3</sub> の混合粉末を焼成後、パルス通電焼結法により焼結体を作製した。

焼結体の電気抵抗(ρ)とSゼーベック係数を測定したところ、ρは、仕込み組成が化学量論組成付近の焼結体では高温ほど減少する半導体的挙動を示した。一方、仕込み組成(SmH<sub>3</sub>/Sm<sub>2</sub>S<sub>3</sub>)が2~2.5以上となりSmH<sub>3</sub>が過剰に

仕込まれると電気抵抗率は金属的な挙動を示した。また、仕込み組成が化学量 論組成付近では温度と共にゼーベック係数が増加する傾向が見られたが、それ よりも SmH<sub>3</sub>を過剰に加えた場合の焼結体ではゼーベック係数の明確な温度依 存性が見られなくなった。出力因子は、Sm過剰の焼結体で1000~1500μWK<sup>-2</sup>m<sup>-1</sup> と化学量論比付近のものに比べると大きくなった。

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#### **Chapter 1 Introduction**

#### 1. 1 Background rare-earth sulfides

Sulfides are promising candidates for environment-friendly and cost-effective materials. The rare-earth elements, Ln, are the elements which atomic numbers are 21, 39 and 57 through 71 in the periodic table. The characteristics of rare-earth elements are unfilled and filled 4f shell and lanthanide contraction.

Rare-earth, Ln, can combine with sulfur to procedure rare-earth sulfides with different formulas, such as rare-earth sesquisulfide ( $Ln_2S_3$ ), monosulfide (LnS),  $Ln_3S_4$ , and  $LnS_2$ .

1.1.1 Structure and characters of rare earth sulfide

Lanthanide monosulfides, LnS, adopt the cubic NaCl-type structure. Magnetic measurements show that most rare-earth monosulfides contain trivalent metals implying an unbonded electron,  $Ln^{3+}(e)S^{2-}$ . The extra electron is delocalized in the 5d conduction band giving rise to metallic type conduction. However, the monosulfide of ytterbium, europium and samarium contain divalent metals, Ln<sup>2+</sup>S<sup>2-</sup>, and behave as semiconductors [1]. The variation of the lanthanide oxidation state is a result of the change of lanthanide electronic configuration. Although the valence configuration of most gas phase  $Ln^{2+}$  ions is  $4f^{n+1}$ , it appears that in some divalent lanthanide compounds, the 4f<sup>n</sup>5d<sup>1</sup> configuration is more stable resulting in an electron occupying the broad 5d band [2, 3]. This is also reflected in their cell parameters, with the genuine  $Ln^{2+}S^{2-}$  compounds having larger cell dimensions than  $Ln^{3+}(e^{-})S^{2-}[4]$ . The lanthanides that usually remain divalent in their compounds are those that have relatively accessible divalent state (i.e. Eu, Yb, and Sm). Generally, the stability of their divalent state increases with decreasing anion electronegativity. These divalent lanthanide compounds varied the lanthanide oxidation state leading to the change in the lanthanide electronic configuration.

Lanthanide sesquisulfides, Ln<sub>2</sub>S<sub>3</sub>, exist in a variety of polymorphic forms and larger lanthanides favoring higher coordination[5]. For a limited range of lanthanide elements, Light Ln<sub>2</sub>S<sub>3</sub> (light Ln: La, Pr, and Nd) exhibit three polymorphic forms ( $\alpha$ ,  $\beta$ and  $\gamma$ ) structure types where the lanthanides are 7- to 8-coordinate [6]. The orthorhombic  $\alpha$ -Ln<sub>2</sub>S<sub>3</sub> is stable at low temperature with exactly stoichiometric and irreversibly transformed to  $\beta$  phase. The tetragonal  $\beta$ -Ln<sub>2</sub>S<sub>3</sub> is an oxysulfide with a limiting composition of Ln<sub>10</sub>S<sub>14</sub>O. Moreover, the  $\beta$  phase is transformed to  $\gamma$  phase with Th<sub>3</sub>P<sub>4</sub> structure at higher temperature. This cubic  $\gamma$  phase has a wide composition range varying from Re<sub>2</sub>S<sub>3</sub> to Re<sub>3</sub>S<sub>4</sub>. In addition, the  $\gamma$  phase exists in all sesquisulfides from La to Lu [7-9]. The composition of  $\gamma$  phase is expressed by R<sub>2.67</sub>V<sub>0.33</sub>S<sub>4</sub> (V: vacancy, where V<sub>0.33</sub> represents the maximum number of metal vacancies); the vacancy can be occupied by an R composition up to R<sub>3</sub>S<sub>4</sub> (R<sub>2.25</sub>S<sub>3</sub>)[6]. The sesquisulfides of Dy to Tm (Lu) exist in the monoclinic  $\delta$ -phase with 6- and 7- coordinate lanthanide ions [10, 11]. The heavier lanthanides (Tm to Lu) typically give sesquisulfides of the  $\epsilon$ -form, having the rhombohedral corundum-type structure, with the lanthanides being 6-coordinate[12]. Low temperature varieties of these sesquisulfides exist in the cubic Tl<sub>2</sub>O<sub>3</sub>-type  $\tau$ -phase[13].

#### 1.1.2 Synthesis of Rare-earth sulfides

Both the monosulfide and sesquisulfides can be obtained from direct combination of elements in stoichiometric properties held at temperature range from 600 to 1050 °C for 2 to 3 days [14]. The monosulfides can be synthesized from their corresponding sesquisulfides through a variety of ways: (1) reduction in the pressure of aluminum (~1500 °C)[15], (2) reaction with lanthanide metal (1350 °C) [16], and (3) thermal dissociation under vacuum (1650 °C)[17].

Cerium, the most fascinating member of the periodic and abundant resources among rare earth elements, is an antiferromagnetic or a superconductor under various conditions of temperature and pressure[18]. My supervisor Professor Hirai had synthesized cerium monosulfide (CeS) powders by the reduction of Ce<sub>2</sub>S<sub>3</sub> powder with an excess amount of metallic Ce at 1273 K for 10.8 ks[15]. Ce<sub>2</sub>S<sub>3</sub> was obtained from with CS<sub>2</sub>-gas sulfurization of ceria (CeO<sub>2</sub>) powder[19]. The synthetic CeS powders contained a small amount of Ce, Ce<sub>2</sub>O<sub>2</sub>S, and  $\beta$ -Ce<sub>2</sub>S<sub>3</sub> as impurities[15]. The oxygen content of CeS compact gradually decreases as the sintering temperature increases due to the evaporation of the volatile CeO[15].

Single-phase CeS compact was formed by sintering at 2173 K[15]. To evaluate the activation energy for densification of CeS, a CeS powder was prepared by milling an initial sintered compact and was used as an ingredient for hot-press experiments[15]. Densification data during hot-press sintering were analyzed using a kinetic equation, showing that boundary diffusion is a rate-limiting process[15]. The results suggest that this boundary diffusion model can explain well the densification data, with apparent activation energy of 479 kJ·mol<sup>-1</sup>[15].

Rare-earth sesquisulfides can be synthesized by the direct reaction of rare-earth and sulfur in a sealed tube [20] or reductive gas sulfurization of rare-earth oxide[6] or slat (carbonate, sulfate, nitrate and oxalate)[21]. However, there are some problems for the direct reaction method. It is difficult to control the partial pressure of rare earths and sulfur to obtain rare earth sulfides with desired compositions. And then the residual oxysulfide leaves in the products from the oxidation of the rare earth surfaces.

The frequently-used reducing agent is H<sub>2</sub>S gas or CS<sub>2</sub> gas[19, 22]. Figure 1.1 shows temperature dependences of  $\Delta G^{\circ}$  values for the sulfurization reactions of La<sub>2</sub>O<sub>3</sub> powders using CS<sub>2</sub> and H<sub>2</sub>S gases. The temperature dependences of the  $\Delta G^{\circ}$  values for the sulfurization reaction of several rare earth oxide powders using CS<sub>2</sub> and H<sub>2</sub>S gases were calculated from the thermodynamic data. The  $\Delta G^{\circ}$  values of almost all the sulfurization reactions with CS<sub>2</sub> progress at a lower temperature because the  $\Delta G^{\circ}$  values are negative and significantly lower than those of the reactions using H<sub>2</sub>S.



Fig. 1.1 temperature dependences of  $\Delta G^{\circ}$  values for sulfurization reactions of  $La_2O_3$ 

To improve this method, our lab has synthesized some lanthanide sesquisulfides with CS<sub>2</sub>-gas sulfurization of their oxides [6, 19, 23]. In the synthesis of light Ln<sub>2</sub>S<sub>3</sub> via the CS<sub>2</sub>-gas sulfurization of Ln<sub>2</sub>O<sub>3</sub> powder, single-phase  $\beta$ -La<sub>2</sub>S<sub>3</sub> were finally synthesized at above 1023 K for 8 h [6]. The  $\alpha$ -Pr<sub>2</sub>S<sub>3</sub> having a trace of  $\beta$ -Pr<sub>2</sub>S<sub>3</sub> was formed for a shorter period of time at above 1123 K[6]. And  $\alpha$ -Nd<sub>2</sub>S<sub>3</sub> having a trace of  $\beta$ -Nd<sub>2</sub>S<sub>3</sub> and single phase  $\alpha$ -Sm<sub>2</sub>S<sub>3</sub> were formed for a shorter period of time at above 1073 and 1123 K, respectively[6].  $Ln_2O_2S$  were also formed in the initial stage of reaction [6]. In all cases, the impurity oxygen content in synthetic powders decreased gradually with an increase in sulfurization temperature. Moreover, the carbon content in these powders increased gradually with an increase in the sulfurization temperature[6].

Single-phase orthorhombic  $\alpha$ -Ln<sub>2</sub>S<sub>3</sub> (Ln= Gd, Tb, and Dy) is prepared at 1023K, 1323 K, 1203 K for 8 h, respectively. Single-phase monoclinic  $\delta$ -Ho<sub>2</sub>S<sub>3</sub> is formed at 1323 K for 8 h [23]. Gadolinium and holmium sesquisulfides were also synthesized via the CS<sub>2</sub>-gas sulfurization of their oxalate, acetate, carbonate, and nitrate[21]. Single phase cubic  $\gamma$ -Gd<sub>2</sub>S<sub>3</sub> was formed by the sulfurization of octanoate at 1073 K and oxalate at 873 K[21]. It has also found that gadolinium salts are thermally decomposed at temperatures high than 500 K[21]. The thermal decomposition leads to the formation of gadolinium oxide via an oxycarbonate. In the case of holmium sesquisulfides, the sulfurization of holmium oxide and nitride provide the mixture of  $\delta$ -Ho<sub>2</sub>S<sub>3</sub> and Ho<sub>2</sub>O<sub>2</sub>S impurity, while pure  $\gamma$ -Ho<sub>2</sub>S<sub>3</sub> is exclusively formed from oxalate, acetates, or carbonates[21]. These results reveal that the formation of oxycarbonate such as Gd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and Ho<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> play an important role in the formation of  $\gamma$ -Gd<sub>2</sub>S<sub>3</sub> and  $\gamma$ -Ho<sub>2</sub>S<sub>3</sub> phase was stable at 1773 K[21].

To reduce the residual carbon content in the synthetic rare earth sulfides prepared by  $CS_2$ -gas sulfurization, especially at higher temperatures, the thermal decomposition of NH<sub>4</sub>SCN was employed as the sulfur source. According to the thermogravimetry-differential thermal analysis (TG-DTA) and mass spectrometry analysis, NH<sub>4</sub>SCN decomposed to NH<sub>3</sub>, CS<sub>2</sub>, H<sub>2</sub>S, and HNCS at 400-550 K with a large mass reduction and endothermic peak [24].

Figure 1.2 shows schematics of the sulfurization apparatus. Different CS<sub>2</sub>-gas sulfurization, the mixture gases from the thermal decomposition of NH<sub>4</sub>SCN were introduced with Ar gas into a silica-glass reaction tube. Single phase of  $\beta$ -La<sub>2</sub>S<sub>3</sub> and  $\beta$ -Gd<sub>2</sub>S<sub>3</sub> were synthesized using these mixture gases from La<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> at 1173 -1373 K. the residual carbon content of the obtained sesquisulfides from NH<sub>4</sub>SCN sulfurization was significantly lower than that of CS<sub>2</sub>-gas sulfurization. So the advantage of NH<sub>4</sub>SCN sulfurization is the decrease of residual carbon content. But the

generated  $H_2S$  gas is too dangerous and the temperature of mantle heater is unstable during the sulfurization process. Therefore, the  $NH_4SCN$  sulfurization is not fit for the industrial production.



Fig. 1.2 Schematics of the sulfurization apparatus

#### 1.1.3 Application,

Rare earth sulfides have been widely used for luminescent[25], magnetic and electronic materials[26]. In the last decade, these materials are essential in the energy storage, energy saving and renewable energy technology, which enable us to realize the sustainable society. Effective application of rare earth sulfides contains three aspects: pigment; crucible; thermoelectric materials.

#### 1.1.3.1 Application of pigment

Rare earth sesquisulfides doping with at least one alkali/alkaline earth metal are well suited for the coloration of cosmetic, plastics, paints and rubbers[27]. Novel environmental friendly colorant/pigment can be prepared via precipitation technology and consisted of a core/shell structure [28]. The core is rare earth sesquisulfides doped with alkali/alkaline earth metal and the shell contains a coating layer of at least one transparent oxide deposited onto the external surface of the doped core particles[28]. The fluorination treatment of the core of doped rare earth sesquisulfide can improve the chromatic (both thermal and chemical stability) properties [29]. Moreover, the mean particle size of colorant products can be controlled with the value of 1.5  $\mu$ m by the variation and optimization of the starting materials and sulfurization agent and condition[30, 31].

New ecological pigment Mg-Yb-S system [32] and Ca-Yb-S system [33]have been synthesized and characterized. MgS-Yb<sub>2</sub>S<sub>3</sub> system[32] gives yellow color while CaS-Yb<sub>2</sub>S<sub>3</sub> system [33] has variable color (blue-green) and controllable crystal structure (NaCl-type and Yb<sub>3</sub>S<sub>4</sub>-type) with different Yb concentration.

Recently, unfilled and sodium doped Ce<sub>2</sub>S<sub>3</sub> with Th<sub>3</sub>P<sub>4</sub> structure, as the most common red paint, has been widely investigated. SiO<sub>2</sub> coated Ce<sub>2</sub>S<sub>3</sub> was prepared as red pigment to improve the thermal stability[34]. Compared with the heavy rare earth ion (Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>) doping of Ce<sub>2</sub>S<sub>3</sub>, the adjacent light rare earth element La was doped to Ce<sub>2</sub>S<sub>3</sub> to improve the stability and check the possibility as red pigment[35]. Moreover, to quest the nontoxic alternatives based on rare-earth elements, the color of cerium fluorosulfide (CeSF, a typical example of the new class of rare-earth pigments) and mercury sulfide  $\alpha$ -HgS (also known as cinnabar red or vermilion) were computed from first principles and the power of modern computational methods implicated the theoretical design of materials with specific optical properties[36].

#### 1.1.3.2 Application of crucible

Another possible application for rare earth sulfide is crucible. Cerium monosulfide with high melting point is possible to consider as a refractory material[15]. Cerium sulfides, CeS, Ce<sub>3</sub>S<sub>4</sub> and Ce<sub>2</sub>S<sub>3</sub>, have been considered as refractory sulfide crucibles[37, 38]. These refractory sulfide crucibles have prepared from the cold-press of the grinded sulfide powders and then sintered with different procedures and technologies[37]. Sulfides powders was prepared by H<sub>2</sub>S gas sulfurization of CeO<sub>2</sub> for Ce<sub>2</sub>S<sub>3</sub>, vacuum heating Ce<sub>2</sub>S<sub>3</sub> near its melting point for Ce<sub>3</sub>S<sub>4</sub> and direct reaction of Ce<sub>2</sub>S<sub>3</sub> and slight excess of Ce for CeS[38].

Test and evaluation of individual sulfide refractory as containers for various metals have been summarized[37]. The operating temperature of CeS crucible is less than 1800 °C and it cannot be used for platinum[37]. The Ce<sub>3</sub>S<sub>4</sub> crucible is more susceptible to reduction of reactive metal for the formation of CeS protective layer and easily attacked by the alkaline earth-metal at its volatile temperature[37]. The properties of Ce<sub>2</sub>S<sub>3</sub> crucible are intermediate between CeS and Ce<sub>3</sub>S<sub>4</sub> so it cannot be used at temperature above 1500 °C[37]. Moreover, the properties of crucible are dependent on the consideration of optimal melting techniques, purification of gas atmospheres and porosity. For a certain metal and sulfide crucible, sometime different

results are obtained. Here, we take titanium and CeS crucible as an example to discuss. When titanium was melted in CeS crucible at 1500 °C for 10 min, sound ingot coated with CeS can be obtained but stuck to crucible. However, Ti melted in CeS crucible with a heavy precipitate. This situation can be explained by three possible elements (porosity, gas atmospheres or melting condition).

#### 1.1.3.3 Application of thermoelectric materials

Excellent thermoelectric materials have a large ZT, which means that the thermopower (S) is large, the electrical resistivity ( $\rho$ ) and the thermal conductivity ( $\kappa$ ) are small. The rough standard for practical use is ZT= 0.8-1. The cubic rare earth sesquisulfides with Th<sub>3</sub>P<sub>4</sub> structure is an important high-temperature thermoelectric material [39].

The solid solution  $Ln_2S_3-Ln_3S_4$  (Ln = La, Ce, Pr, Gd, Dy) with cubic structure have been extensively investigated for high temperature thermoelectric conversion materials. All  $\gamma$ -Ln<sub>2</sub>S<sub>3</sub> compounds are insulator without any vacancy while Ln<sub>3</sub>S<sub>4</sub> has one ninth conduction electron in per formula unit. The content of rare-earth vacancy is dependent on the ration of Ln/S from 1.33 to 1.5. As the quantity of vacancy increases, the n-type carrier concentration increases. Namely, the electron concentration and power factor can be increased by self-doping. Further, the lattice thermal conductivity can be kept low because of the complex crystal structure. Additionally, most rare earth sesquisulfides have melting points of greater than 2000 K. Theoretically speaking; it is possible to optimize the electrical conductivities, carrier concentrations and charge-carrier mobilities by adjusting the vacancy contents.

Actually, we need to consider which specific rare-earth element is the best choice for the highest potential thermoelectric performance before we optimize the vacancy concentrations. However, it is a very difficult problem to answer. Because rare earth elements are similar in properties and the differences of electrons numbers of 4f layer have no direct influence on thermoelectric properties, which is different with magnetic materials. Secondly, the most suitable sulfide is difference from the published data, e.g., Takeshita et al. [40] reported a ZT value of 0.75 for  $LaS_{1.42}$  at 1273 K, while Gadzhiev et al. [41] reported GdS<sub>1.48</sub> has a ZT value of 0.74 at 1200 K. Furthermore, Taher and Gruber [42] estimated a ZT value of 0.41 for NdS<sub>1.49</sub> at 770 K and determined the highest ZT value of 1.5 for DyS<sub>1.496</sub> at 1000 K.

The reasons caused the difference included the following aspects: (1) the influence of impurity content on the thermoelectric property, e.g., if the measured sample contained oxygen contamination or the formed  $\beta$ -phase on the grain boundary of  $\gamma$ -phase, which may cause a concomitant deterioration of the electrical conductivity. (2) The effects of preparation methods. Preparation methods employed by different authors may also cause differences between different stoichiometry. (3) In the calculation process of the above mentioned ZT values, the thermal conductivity is not experimentally determined, but analogy. Because there is the assumption, these ZT values may include some errors. (4) Not only the preparation process may affect the thermoelectric properties, different testing gas atmospheres may also cause slightly changes in the chemical composition, because different gas atmosphere will affect the stability of sample dissociation energy. These variations are so small and little that there is little literature made a detailed characterization of microstructure structure or the composition for the tested sample. According to another expression of ZT, effective mass and mobility are proportional to ZT value. Gadzhiev et al. have compared effective masses and mobilities of La<sub>3</sub>S<sub>4</sub>, Dy<sub>3</sub>S<sub>4</sub>, Pr<sub>3</sub>S<sub>4</sub>, and Gd<sub>3</sub>S<sub>4</sub> and found that La<sub>3</sub>S<sub>4</sub> had large effective mass and mobility. However, Vickery R.C. et al. concluded that the shift point occurred at the Gd in the research of the influence of different chalcogenides and rare earth elements on the thermoelectric properties. So, Gd-based sulfides are also possible for the high performance thermoelectric materials. For the element of Pr or Dy, there is some problem for the hypothesis of calculation of thermal conductivity thermal conductivity (detail analysis process in reference [39]) so these two elements are low probability. After determining the matrix elements, the different doping elements are chosen to optimize the thermoelectric performance for different systems.

Based on the above analysis, our lab chose  $La_2S_3$  and  $Gd_2S_3$  as a matrix. For  $La_2S_3$ , stability was improved by doping different transition metal elements (Ti, Zf) and thermoelectric properties of  $La_2S_3$  were optimized by a novel preparation method. For  $Gd_2S_3$ , ternary and non-stoichiometry method were employed to optimize the carrier concentration and the optimized ZT reached 0.51 at 950 K for NdGd<sub>1.02</sub>S<sub>3</sub>[43].

#### **1.2 Valence-Fluctuation rare-earth sulfides**

1.2.1 Mixed-valence rare-earth sulfide

Mixed-valence or mixed-configuration rare-earth compound and sometime as fluctuating-valence or fluctuating-configuration rare-earth compound are a number of compound with the character of atomic-like f levels and the wide s-d band coexist at the Fermi surface[44]. The nature of fluctuating-valence of rare-earth element is that both the 4f<sup>n</sup> and 4f<sup>n-1</sup> configurations contribute to the intermediate-valence wavefunction[45]. The mixed-valence state can be thought of as a mixture of 4f<sup>n</sup> and 4f<sup>n-1</sup> ions, the energies of which are nearly degenerate[45]. Three elements (pressure, temperature and element substitution) can cause these valence-fluctuation phenomena.

In rare earth systems, elements with valence fluctuation feature involving Ce, Sm, Eu, Tm and Yb, are energetically found to be near each other and can be inverted by externally applied or internally generated constraints. Such inversion involves a change in the valence state of the rare earth ion. In this study, we just studied Yb, Eu, and Sm related sulfides.

#### 1.2.2 Property and structure characteristic of valence change rare-earth sulfide

The archetypal valence instability occurs in FCC samarium monosulfide (SmS) due to the pressure-induced phase transformation from semiconducting to metallic phase [46]. Both lattice parameters and resistances of SmS have an abrupt decrease under the effect of pressure without any change in the crystal structure [46]. The reduction of lattice constant is connected with the diameter of Sm ion because the diameter of bivalent and trivalent Sm ion is 1.14 and 0.96 Å, respectively. The reduction of cell constant is attributed to the partial transformation of Sm<sup>2+</sup> to Sm<sup>3+</sup> resulting from the hybridization of 4f electrons and the 5d conduction band with the decrease of energy gap. The energy band gap of SmS with NaCl structure reduced from 0.2 eV to 0.065 eV following the increase of pressure to around 6.5 kbr [47].

In order to determine the presence or absence of the mixed-valence and electronic structure, semiconductor and metallic SmS were analyzed by optical reflectivity[48] and angle-resolved photoemission spectroscopy[49]. X-ray absorption and resonance photoemission spectroscopy show mixed valency of  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  states in semiconducting SmS at low temperature (T=30 K) and high-resolution temperature-dependent valence-band photoemission spectroscopy show a pseudogap within 20 meV of the Fermi level at low temperatures [50]. In order to further understanding of phase transitions, many SmS-based ternary sulfides were researched.

Other rare earth elements (Y[51, 52], La[53] and Eu[54]) and transition metal elements (nickel [55] and manganese [56]) diffusion in samarium sulfide single crystal, polycrystalline and film were studied to improve the thermovoltaic effect in samarium sulfide based materials.

Europium monosulfide (EuS) is very similar with SmS in crystal structure and atom size. Similar with SmS, EuS also has phase transformation under hydrostatic pressure. The effect of pressure on magnetic transitions of EuS under hydrostatic pressure up to 10 kbars was reported and the magnetic exchange interactions vary in an important way with volume [57]. The behavior of EuS under pressure is an example of the competition between a structural NaCl-CsCl transition and f - d mixing[58].

EuS, as the ideal Heisenberg ferromagnet, had attracted sustained interest as the model crystals for investigations of magnetism in magnetic semiconductors[59]. In NaCl structure of EuS, only nearest-neighbor  $J_1$  and next-nearest-neighbor  $J_2$  exchange interactions are important[60]. the exchange-parameter  $J_1$  and  $J_2$  are in essential agreement with the inelastic-neutron-scattering but in marked disagreement with Swendsen's Green's-function theory and its application to the calculation of the ferromagnetic and paramagnetic Curie temperature[60].

Electron-beam-excited luminescence spectra for EuS show a series of low-energy broad corresponding to 4f<sup>7</sup>-4f 6<sup>5</sup>d transition and high-energy sharp peaks arising from intra-atomic transitions within the 4f configuration in the Eu ions [61]. A proposed energy level diagram for EuS has been derived previously from the optical data [62]. A slight indication of two crystal-field split 5d subbands can be deduced from the calculated density of states of EuS [62]. EuS microcrystal-embedded oxide thin films [63]and novel EuS nanocrystal containing paramagnetic Mn(II), Co(II), or Fe(II) ions [64] were prepared and their effective optical Faraday effects were investigated.

Specific heat measurements of EuS between 10 K and 35 K show a sharp peak at 16. 2 K and the dominant exchange interaction is between nearest neighbor Eu<sup>2+</sup> ions [65]. The ferromagnetic Curie temperature of EuS increases linearly for hydrostatic pressures up to 4 kbar at a rate of 0.28 K/kbar because the interaction of the magnetic moments in EuS depends much stronger on the volume than the common superexchange mechanism [66]. The variation of specific heat is connected with the isothermal entropy change so it is meaningful to test the magnetic and thermal

properties of EuS for the possible application of magnetic refrigerant materials, which is based on the isothermal entropy change induced by the variation of an applied magnetic field [67]. The high magnetocaloric effect of EuS, as compared to the usual  $Gd_3Ga_5O_{12}$ , made it as a first candidate for a low field refrigeration cycle (~ 1T)[67].

YbS differed from SmS and EuS by the presence of hole-type conduction and the energy band structure of YbS can be determined with the optical investigations[68]. Diffusive reflection spectra of YbS powders had a step due to electronic transitions with energies near 1.2 eV[68]. The optical-absorption band gap of YbS due to the lowest 4f- 5d transition has been studied as a function of pressure and the rate of closure of this gap with pressure lead to a metal-semiconductor transition in YbS [69]. The optical response and lattice-parameter measurements indicated the onset of a 4f-shell instability near 100 kba [70]. In these above mentioned researches, the influence of pressure on the stability and band structure of YbS had been researched.

In the metallic and semiconductor SmS, both bivalent and trivalent Sm ions had the crystallographic equivalence of the cation sites and a metallic like conductivity band is present near the Fermi energy. Moreover, a thermally activated hopping of the charge carriers occurred for Eu<sub>3</sub>S<sub>4</sub> and Sm<sub>3</sub>S<sub>4</sub> with the Th<sub>3</sub>P<sub>4</sub> structure. However, cations with different valence in Yb<sub>3</sub>S<sub>4</sub> occupy inequivalent lattice site so the valence distribution is static and no fluctuation is possible. The energy gaps of Sm3S4 are similar with these of SmS and its band conduction involved a thermal activation of charge carriers and a hopping conduction with temperature dependence frequency factor [71].

1.2.3 Research and application of valence change rare-earth sulfide

Similar with other heavy rare-earth sulfides, there is little research about preparation and characterization of ytterbium monosulfide. SmS based film can be employed as strain-sensing layer of resistant strain gauge. This application is based on the sensitivity of SmS under pressure. On the other hand, SmS based sulfides are expected to be employed as high temperature thermoelectric materials. Kazanin M. M. et al.[72] have optimized thermal electromotive force by slightly variation and control of composition or rare-earth/transition element doping. The mechanism of the formation of thermal electromotive force and influence elements were investigated. The study of EuS is focus on the preparation and characterization of nano-size

material to improve the magnetic and optical properties.

#### **1.3 Research purpose and motivation**

The reasons for the study of rare earth sulfides were listed in below:

(1) Sulfides are promising candidates for environment-friendly and cost-effective functional materials [73]. The extensive research devoted to the physics and chemistry of rare-earth sulfides during the end of the last century has led to great advances the understanding of the properties of solids in general.

(2) Several years ago, the demand for rare earths is expected to increase because of their expansion into the fields of high-performance motors and automotive exhaust catalysts. However, serious overcapacity is a long-standing problem in China's rare earths market. China's expanding economy is posing a risk to supply of REEs worldwide [74].

(3) The physical properties of rare-earth compounds are essentially influenced by the rare earth's 4f electrons[75]. Among the rare-earth compounds there is a fascinating class of solids called intermediate (or homogeneously mixed) valence compounds [75]. To develop the novel application for sulfide related compound is meaningful and important.

(4) Mixed-valence rare earth sulfides had special electrical structures and then possessed many potential applications.

In this task, we dedicated to research on the following topics;

(1) Research of preparation and sulfurization technology of valence fluctuation rare-earth sulfides. In order to achieve industrial production of rare earth sulfides, it is necessary to study the influence of characteristics of starting material on the sulfurization process. Meanwhile, we need to further optimize the sulfurization process based on the former researches. Compared with light rare earth sulfides, crystal structures of heavy rare earth sulfides are more complex. Moreover, there are some difficulties on the preparation of heavy rare earth sulfides, especially for Yb and Lu in our lab. Therefore, this study chose ytterbium sulfide with characteristics of valence fluctuation state as the initial study content. We employed four kinds of Yb<sub>2</sub>O<sub>3</sub> with different specific surface area, grain size and particle size distributions as starting materials, systematically researched the influences of sulfurization temperature, sulfurization time, gas-flowing rate, and different sulfurization programs on the

sulfurization products. We wish to understand the influence of characteristics of starting material on the sulfurization processes. Meanwhile, raw materials with different characteristics can be obtained optimal process parameters in order to provide a meaningful reference for future industrial production. The sulfurization process of  $Eu_2O_3$  is different with other rare earth sulfide because there is no  $Eu_2S_3$ . Therefore, it is meaningful to systematically study the sulfurization process of  $Eu_2O_3$ .

(2) Research of phase transformation processes and sintering for mixed-valence rare earth sulfides. Stability of rare earth sulfides is defining factors of rare earth sulfides during industrialization application. Stability of rare earth sulfides is connected with dissociation energy on the surface layer of sulfide, so the vapor pressure of sulfur affected the stability of rare earth sulfide and phase transformation processes. In this study, synthetic ytterbium sulfides and europium sulfides were treated under different atmospheres to study their stability and phase transformation. We also researched the sintering process for valence fluctuation rare earth sulfides.

(3) Novel and possible application of valence fluctuation rare earth sulfide

For the application of rare earth sulfide, we should consider the different characteristics for different rare earth elements and compounds and then choose different application fields. How to choose the application of rare earth sulfides? What factors need to be considered?

We take EuS as an example. To store and transport hydrogen fuel, it is effective to liquefy hydrogen; therefore, a magnetic refrigerant material with a large specific heat near the liquid hydrogen temperature is required. Near the liquid helium temperature, medium and heavy rare-earth compounds exhibiting large specific heats due to magnetic phase transitions and possessing large total angular momentum quantum numbers are at the level practically required of magnetic refrigerant materials. However,  $Er_3Ni$  and  $HoCo_2$  have minimum specific heat values near the liquid hydrogen temperature, and oxysulfides that contain heavy rare-earth elements and possess specific heat peaks have small specific heats near the liquid hydrogen temperature. Recently, we discovered that polycrystalline EuS, which also contains a bivalent cation ( $Eu^{2+}$ ), has a large specific heat peak (0.7 J·K<sup>-1</sup>·cm<sup>-3</sup>) near 16.5 K, which is the liquid hydrogen temperature. So, it is interesting and meaningful to research the possibility for EuS as novel magnetic refrigerant material for liquid

hydrogen.

Different with YbS and EuS, SmS has small resistivity, so it is possible to be used as high temperature thermoelectric materials. It is expected to optimize the thermoelectric properties by controlling the composition.

Not every valence fluctuation rare earth sulfides (even rare earth sulfide) can find a suitable or possible new application. Such as ytterbium sulfide, it is not fitting for thermoelectric materials due to large resistivity and magnetic refrigerant material. It need further explore for its application.

#### Chapter 2 Synthesis, sintering and heat capacity of ytterbium sulfides

#### **2.1 Introduction**

Rare-earth sulfides have been considered as the candidate for pigments [36, 76, 77], high temperature thermoelectric materials [22, 43], refractory materials [15] and optical materials [78]. Ytterbium sulfides have received considerable attentions for their interesting thermoelectric properties [79] and optical properties. Especially, ytterbium monosulfide (YbS) has been researched as high temperature thermoelectric materials for its p-type electrical conductivity while most rare earth chalcogenides have n-type electrical conductivity [79]. Furthermore, YbS is also expected to be used as refractory materials for its high melting point (2130°C) [80].

In former studies, binary rare-earth sesquisulfide  $Ln_2S_3$  (Ln = rare-earth element) had been formed via the sulfurization of their oxides or salts under CS<sub>2</sub> gas [19, 21, 81, 82]. Moreover, some remarkable breakthroughs have been made on thermoelectric properties of non-stoichiometric ternary and quaternary rare-earth sulfides (LaGd<sub>1+x</sub>S<sub>3</sub> [22], SmGd<sub>1+x</sub>S<sub>3</sub> [22], SmEuGdS<sub>4</sub> [83], NdGd<sub>1+x</sub>S<sub>3</sub> [43]) by tuning their chemical compositions with rare-earth element self-doping [84]. These investigations imply the preparations of Ln<sub>2</sub>S<sub>3</sub> with CS<sub>2</sub> gas become feasible at lower temperature in comparison with the sulfurization of H<sub>2</sub>S gas [85]. The volatile liquid CS<sub>2</sub> is easier to handle for its less toxic compared with H<sub>2</sub>S [86]. However, there is no report about the influences of particle size and specific surface area (denoted as SSA hereafter) of Ln<sub>2</sub>O<sub>3</sub> on sulfurization process via CS<sub>2</sub> gas.

In literature [80], the sulfurization temperature of 1250 °C is too high for the synthesis of  $Yb_2S_3$ . Partial  $CS_2$  molecular decomposed to carbon. Residual carbon affects the color of products, which limited its application as pigment materials. It is necessary to study the possibility of preparing  $Yb_2S_3$  at lower temperature by controlling  $Yb_2O_3$  characters or sulfurizing  $Yb_2O_3$  in proper  $CS_2$  gas flow rate (denoted as GFR hereafter) to lessen residual carbon content.

Different with light rare-earth sesquisulfides, heavy rare-earth sesquisulfide Yb<sub>2</sub>S<sub>3</sub> has several polymorphic forms. Hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> [87] transforms into monoclinic  $\delta$ -Yb<sub>2</sub>S<sub>3</sub> at 897 °C [12]. Cubic  $\phi$ -Yb<sub>2</sub>S<sub>3</sub> with lattice parameter *a*=10.3 Å transforms into Th<sub>3</sub>P<sub>4</sub>-type  $\gamma$ -Yb<sub>2</sub>S<sub>3</sub> at a higher temperature [12]. In spite of the extensive polymorphisms in Yb<sub>2</sub>S<sub>3</sub>, the above transformations are not presented in the Yb-S phase diagram [12] with the pressure of 4.5 atmospheres [88]. These phase

transformations and sulfurization products are dependent on reaction condition, e. g.,  $Yb_3S_4$  phase has been synthesized by the sulfurization of  $Yb_2O_3$  at 1300 °C via H<sub>2</sub>S gas [89]. Is it achievable to obtain different polymorphic  $Yb_2S_3$  by control sulfurization condition?

In Yb-S binary system, polymorphic Yb<sub>2</sub>S<sub>3</sub>, Yb<sub>3</sub>S<sub>4</sub>[89, 90] and YbS [91] had been checked by electron diffraction. Different with light rare-earth sesquisulfides, Yb<sub>2</sub>S<sub>3</sub> has several polymorphic forms. Hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> [87] transforms into monoclinic  $\delta$ -Yb<sub>2</sub>S<sub>3</sub> at 897 °C [12]. Cubic  $\phi$ -Yb<sub>2</sub>S<sub>3</sub> with lattice parameter *a*=10.3 Å transforms into Th<sub>3</sub>P<sub>4</sub>-type  $\gamma$ -Yb<sub>2</sub>S<sub>3</sub> at a higher temperature [12]. These phase transformations and sulfurization products are dependent on reaction condition, e. g., Yb<sub>3</sub>S<sub>4</sub> phase has been synthesized by the sulfurization of Yb<sub>2</sub>O<sub>3</sub> at 1300 °C via H<sub>2</sub>S gas [89]. Is it achievable to obtain different polymorphic Yb<sub>2</sub>S<sub>3</sub> by control sulfurization condition? Moreover, there is little report about the synthesis of ytterbium sulfides, whether Yb<sub>3</sub>S<sub>4</sub> or YbS, by heat treatment of Yb<sub>2</sub>S<sub>3</sub> under different atmospheres.

#### 2.2 Experimental details

#### 2.2.1 Characters of Yb<sub>2</sub>O<sub>3</sub> powders

Herein, Yb<sub>2</sub>O<sub>3</sub> powders provided by different companies (specific surface area 50 m<sup>2</sup>/g, purity 99.8%, Shin-Etsu Chemical Co., Ltd., remarked as Yb<sub>2</sub>O<sub>3</sub>-A; specific surface area 10 ~ 25 m<sup>2</sup>/g, purity 99.9%, mean particle size 0.5 ~ 2  $\mu$ m, NIPPON Yttrium Co., Ltd., remarked as Yb<sub>2</sub>O<sub>3</sub>-B; particle size 0.37  $\mu$ m, purity 99.8%, Shin-Etsu Chemical Co., Ltd., remarked as Yb<sub>2</sub>O<sub>3</sub>-C; specific surface area 2 m<sup>2</sup>/g, particle distribution 3 ~5  $\mu$ m, purity 99.99%, Shin-Etsu Chemical Co., Ltd., remarked as Yb<sub>2</sub>O<sub>3</sub>-C; specific surface area 2 m<sup>2</sup>/g, particle distribution 3 ~5  $\mu$ m, purity 99.99%, Shin-Etsu Chemical Co., Ltd., remarked as Yb<sub>2</sub>O<sub>3</sub>-D) were examined.

Figure 2.1 shows SEM microstructure of ytterbia powders with different SSA and particle size. Yb<sub>2</sub>O<sub>3</sub>-A particle has bigger SSA (Table 2.1) and irregular shape (Figure 2.1a). Compared with Yb<sub>2</sub>O<sub>3</sub>-A, Yb<sub>2</sub>O<sub>3</sub>-B has smaller particle size (Figure 2.1b) and SSA. Homogeneous spherical particle of Yb<sub>2</sub>O<sub>3</sub>-C has a uniform size of ~ 0.37um (Table 2.1 and Figure 2.1c). Polygonal tabular particle of Yb<sub>2</sub>O<sub>3</sub>-D is different with others Yb<sub>2</sub>O<sub>3</sub> and has bigger particle (Figure 2.1d) and smaller SSA (Table 2.1).

Figure 2.2 shows particle size distribution of  $Yb_2O_3$  powders. The average particle size of  $Yb_2O_3$ -A is 3.92 µm. The distribution of  $Yb_2O_3$ -B reflects a broad range of particle sizes with poor uniformity. Due to the large proportion of particles

below 1 micron in size (Figure 2.1), Yb<sub>2</sub>O<sub>3</sub>-B would have a reunion. The first peak corresponds Yb<sub>2</sub>O<sub>3</sub>-B primary particles with particle size of ~ 1 $\mu$ m. The agglomerate of Yb<sub>2</sub>O<sub>3</sub>-B causes average particle size of second particle (7.89 $\mu$ m) is larger than that showed in Figure 2.1b. The particle size distribution of Yb<sub>2</sub>O<sub>3</sub>-C contains two parts. The left part is primary particle distribution and right part is aggregated particle distribution. For Yb<sub>2</sub>O<sub>3</sub>-D, the average particle size is large (8.68 $\mu$ m) as showed in Figure 2.1d.

Raw material	SSA(m <sup>2</sup> /g)	Size(µm)	Purity (%)	Producer
Yb <sub>2</sub> O <sub>3</sub> -A	50	~1	99.8	Shin-Etsu Chemical Co., Ltd.,
Yb <sub>2</sub> O <sub>3</sub> -B	10~25	0.5 ~ 2	99.9	NIPPON Yttrium Co., Ltd.,
Yb <sub>2</sub> O <sub>3</sub> -C	13.31	0.37	99.8	Shin-Etsu Chemical Co., Ltd.,
Yb <sub>2</sub> O <sub>3</sub> -D	2	3 ~ 5	99.99	Shin-Etsu Chemical Co., Ltd.,

Table 2.1 Information of Yb<sub>2</sub>O<sub>3</sub> powders with different characteristic



Figure 2.1 SEM images of Yb<sub>2</sub>O<sub>3</sub>-A (a), Yb<sub>2</sub>O<sub>3</sub>-B (b), Yb<sub>2</sub>O<sub>3</sub>-C (c), Yb<sub>2</sub>O<sub>3</sub>-D (d).



Figure 2.2 Particle size distributions of Yb<sub>2</sub>O<sub>3</sub> powders 2.2.2 Sulfurization, heat treatment and sintering of ytterbium sulfides

The sulfurization experiment was conducted via the following procedure. A silica boat loaded with Yb<sub>2</sub>O<sub>3</sub> was inserted into a silica-glass tube in the furnace (ARF3-500-60KC, Asahi Rika Mfg. Co., Ltd.) and then the pressure in the tube was pumped into less than 0.1 Pa. After the tube was filled with argon gas, the boat was heated to setting temperature (500 ~ 1050 °C). Reagent-grade liquid CS<sub>2</sub> (Kanto Chemical Co., Tokyo, Japan) was carried into the reactor by flowing carrier argon gas through a bubbler in a flow rate of 0.83 mL/s ~ 3.33 mL/s. The sulfurization experiments were continued up to 0.5 ~ 8 hr. The reactor system was cooled to room temperature in a stream of Ar gas.

The heat treatments of synthetic Yb<sub>2</sub>S<sub>3</sub> contain three conditions; 1) 1000 ~1050 °C for 3 hr ~ 12 hr under Ar/CS<sub>2</sub> or Ar gas: three grams of synthetic Yb<sub>2</sub>S<sub>3</sub> were treated with the same apparatus for sulfurization. 2) 1000 ~1500 °C for 1 hr ~ 5 hr under vacuum less than  $1.2 \times 10^{-3}$  Pa: above one grams of synthetic single orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> or hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> was placed on a BN boat (inner diameter of 15 mm) and inserted into an alumina tube. The reactor system was heated to 500-1550 °C with 10 °C/min. 3) Closed system: synthetic Yb<sub>2</sub>S<sub>3</sub> was placed in a graphite die (inner diameter of 10.5 mm) and cold pressed under a uniaxial applied

stress of 25 MPa. And then it was sintered at 1000 ~ 1400 °C with heating rates of 0.42 K·s<sup>-1</sup> under 50 MPa by spark plasma sintering (Model SPS-511L, Sumitomo Coal Mining Co. Ltd, Tokyo, Japan). The sintering vacuum is lower than  $7 \times 10^{-3}$  Pa. And then synthetic Yb<sub>3</sub>S<sub>4</sub> or YbS powders were sintered at 1000°C-1900 °C for 1- 5 hr under 50 MPa by spark plasma sintering.

2.2.3. Analysis and characterization of as-synthesized materials

X-ray diffraction (XRD, Model Rint-Ultima+, Rigaku Corp., Tokyo, Japan) with monochromatic Cu K $\alpha$  radiation at 40 kV and 20 mA was applied to check phase compositions of sulfurization products and polymorphic forms of Yb<sub>2</sub>S<sub>3</sub>. Cell parameters of synthetic powders were measured with the scan step of  $1.0 \times 10^{-3}$  degree for 2s. The reaction degree was estimated from the normalized intensities of the diffraction lines of each reaction product. Morphology of synthetic Yb<sub>2</sub>S<sub>3</sub> was characterized by scanning electron microscopy (SEM, JSM-5310LV, JEOL Ltd. Tokyo, Japan) to study the change of Yb<sub>2</sub>O<sub>3</sub> powders before and after sulfurization. The effect of impurity content on particle size of Yb<sub>2</sub>S<sub>3</sub> powders was also studied.

Chemical compositions of synthetic powders were measured by oxidizing them to stoichiometric Yb<sub>2</sub>O<sub>3</sub>. And 0.2~0.5 g of each powder was placed in a quartz crucible and inserted into an electric furnace. The powders were heated to 1000 °C for 3 hr with heating rate of 0.37 °C·s<sup>-1</sup> and subsequently cooled to room temperature in air. The thermal analysis showed that Yb<sub>2</sub>S<sub>3</sub> was completely oxidized to Yb<sub>2</sub>O<sub>3</sub> at 800 °C. Ytterbium (Yb) content and sulfur (S) content were calculated from the weight of Yb<sub>2</sub>O<sub>3</sub> and weight change caused by the complete oxidation of the sulfide to the oxide. The oxygen content and carbon content of synthetic powders were determined by an oxygen determinator (Model TC-436, LECO Corp., St. Joseph, MI) and a carbon determinator (Model CS-444LS, LECO Corp., St. Joseph, MI), respectively.

SSA of synthetic  $Yb_2S_3$  was measured by a surface area and pore size analyzer (AUTOSORB-1, QUANTACHROME INSTRUMENTS, Florida, USA) using the Multi-point Brunauer, Emmett and Teller (BET) method with  $N_2$  adsorption to indirectly reveal particle size of sulfurization product. Particle size distributions of  $Yb_2O_3$  and  $Yb_2S_3$  were measured by laser diffraction particle size distribution analyzer (Nikkiso Co, Ltd., Japan).

The thermal-relaxation technique was employed for specific heat measurement

in the temperature range between 2 and 100 K by using a physical properties measurement system (PPMS, Quantum Design).

#### 2.3 Sulfurization of ytterbium sesquisulfides

In this study, four kinds of Yb<sub>2</sub>O<sub>3</sub> powders with different characters (remarked as Yb<sub>2</sub>O<sub>3</sub>-A~D, detail informations listed in Table 1) were sulfurized via CS<sub>2</sub> gas to investigate the influence of Yb<sub>2</sub>O<sub>3</sub> characters on fabrication of single Yb<sub>2</sub>S<sub>3</sub> phase. The chemical compositions of sulfurization products were measured. Dependences of temperature on the formation of Yb<sub>2</sub>S<sub>3</sub> were systematically researched. Morphology and SSA of sulfurization products were characterized. Based on experimental results, the elements on sulfurization reaction rate were discussed and synthesis process of Yb<sub>2</sub>S<sub>3</sub> was compared with that of light Ln<sub>2</sub>S<sub>3</sub>.

#### 2.3.1 XRD results of Yb<sub>2</sub>S<sub>3</sub>

Figure 2.3 shows representative XRD patterns of synthetics with sulfurization at 600 ~1050 °C for 0.5 ~ 8 hr and GFR of 1.67 mL/s. In Figure 2.3a, a new polymorphic form of Yb<sub>2</sub>S<sub>3</sub> (named  $\eta$ -Yb<sub>2</sub>S<sub>3</sub>) formed by the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-A at 600°C for 8 hr. This  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> poses similar XRD pattern and lattice plane (Table 2.2) with those of  $\eta$ -Lu<sub>2</sub>S<sub>3</sub> with orthorhombic structure [92], which has a space group of Fddd (Sc<sub>2</sub>S<sub>3</sub> type)[93]. Single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> can be gained at 600 ~ 900 °C for Yb<sub>2</sub>O<sub>3</sub>-A. Hexagonal Yb<sub>2</sub>S<sub>3</sub> phase (named  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub>) formed at 1000 °C for 1 hr. For higher sulfurization temperature of 1050 °C, the intensities of  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> characteristic peaks strengthened while those of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> weakened. Moreover, the mass content of  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> is 20.9% at 1000 °C for 1 hr and 57.8% at 1050 °C for 0.5 hr, respectively.

For the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-B, single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> phase appeared at 700 °C for 4 hr. Different with the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-A,  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase formed at 800 °C for 3 hr with the mass content of 4.88%. The  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> becomes main phase with the mass content of 75.7% and weak peaks of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> have been perceived simultaneously at 900 °C for 2 hr. The products completely translated into  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase at 1000 °C for 1 hr. Single  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase can be obtained for a short sulfurization time of 0.5 hr at 1050 °C.

In the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-C, the formation temperature of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> or  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> is similar with that of Yb<sub>2</sub>O<sub>3</sub>-B. Small amount of  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase formed at 900 °C, which is lower than that of Yb<sub>2</sub>O<sub>3</sub>-A (1000°C). The content of  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase increased following temperature increase. Single  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase can be gained with

the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-C at 1000  $^\circ C$  for 1 hr and 1050  $^\circ C$  for 0.5 hr.

Different with the former sulfurization results,  $Yb_2O_2S$  appeared as a transitional product for the sulfurization of  $Yb_2O_3$ -D.  $Yb_2O_2S$  and  $\epsilon$ - $Yb_2S_3$  phase coexisted at 950 ~ 1050 °C for 3 ~ 8 hr. Moreover, the intensities of characteristic peaks of  $\epsilon$ - $Yb_2S_3$  obviously added while those of  $Yb_2O_2S$  decreased following temperature increase.

Miller indices		d-spacin	ng (nm)	Intensity		
h	k	1	$Yb_2S_3$	$Lu_2S_3$	$Yb_2S_3$	$Lu_2S_3$
1	1	1	0.60856	0.60445	65	49
0	0	4	0.57703	0.57182	10	7
0	2	2	0.49111	0.48732	14	11
1	1	5	0.37254	0.3695	30	18
2	0	2	0.36747	0.3651	5	5
1	3	1	0.3246	0.32225	15	11
2	2	0	0.31544	0.31337	44	38
0	2	6	0.31384	0.31118	40	37
1	1	7	0.29222	0.28974	7	7
0	0	8	0.28851	0.28591	3	2
2	2	4	0.27678	0.27481 8		5
2	0	6	0.27306	0.27098 100		100
0	4	0	0.27135	0.26934	50	49
1	3	5	0.2673	0.26521	11	7
3	1	1	0.24993	0.24836	6	6
0	4	4	0.24555	0.24366	3	2
1	3	7	0.23249	0.23061	3	4

Table 2.2 X-ray diffraction patterns for  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and  $\eta$ -Lu<sub>2</sub>S<sub>3</sub>





Figure 2.3 XRD patterns of samples produced by the sulfurization of  $Yb_2O_3$ -A (a),  $Yb_2O_3$ -B (b),  $Yb_2O_3$ -C (c) and  $Yb_2O_3$ -D (d) with gas flow rate of 1.67 mL/s.

Chemical compositions of sulfurization products with GFR of 1.67 mL/s are listed in Table 2.3. Yb content of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> is close to 78.28%, which suggests this  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> is an isomer of Yb<sub>2</sub>S<sub>3</sub>. For Yb<sub>2</sub>O<sub>3</sub>-B, the minimum of impurity content of 0.02% grained at 1050 °C for 0.5 hr while the minimum of impurity content is 0.06% for Yb<sub>2</sub>O<sub>3</sub>-C sulfurized at 1000 °C for 1 hr.

Starting materials	Sulfurization		Product	Composition (mass %)		
Starting materials	°C	hr	Troduct	Yb	S	Impurity
Yb <sub>2</sub> O <sub>3</sub> -A	1050	0.5	$M-Yb_2S_3$	77.88	21.61	0.52
Yb <sub>2</sub> O <sub>3</sub> -B	700	4	$\eta$ -Yb <sub>2</sub> S <sub>3</sub>	78.69	20.79	0.52
Yb <sub>2</sub> O <sub>3</sub> -B	800	3	$M-Yb_2S_3$	78.53	21.15	0.32
Yb <sub>2</sub> O <sub>3</sub> -B	900	2	$M-Yb_2S_3$	78.23	21.70	0.07
Yb <sub>2</sub> O <sub>3</sub> -B	1000	1	ε-Yb <sub>2</sub> S <sub>3</sub>	77.87	21.61	0.53
Yb <sub>2</sub> O <sub>3</sub> -B	1050	0.5	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.30	21.69	0.02
Yb <sub>2</sub> O <sub>3</sub> -C	900	2	$M-Yb_2S_3$	78.53	21.16	0.31
Yb <sub>2</sub> O <sub>3</sub> -C	1000	1	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.32	21.62	0.06
Yb <sub>2</sub> O <sub>3</sub> -C	1050	0.5	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.57	21.05	0.37

Table 2.3 Chemical composition of Yb<sub>2</sub>S<sub>3</sub> with gas flow rate of 1.67 mL/s

Theory value  $W_{Yb}$ = 78.28%; Ws= 21.72%; M-Yb<sub>2</sub>S<sub>3</sub>: mixture of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub>.

#### 2.3.2 Dependence of temperature, time and GFR on the formation of Yb<sub>2</sub>S<sub>3</sub>

Figure 2.4 shows temperature dependences of diffraction intensity of Yb<sub>2</sub>O<sub>3</sub> (222), Yb<sub>2</sub>O<sub>2</sub>S (011),  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> (206) and  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> (110) formed via the sulfurization of Yb<sub>2</sub>O<sub>3</sub> at 700 °C ~ 1000 °C for 1 hr and 3 hr with GFR of 1.67 mL/s. The reaction sequence is Yb<sub>2</sub>O<sub>3</sub> $\rightarrow$ Yb<sub>2</sub>O<sub>2</sub>S $\rightarrow$  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> $\rightarrow$   $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> with increasing temperature. However, there is no intermediate product Yb<sub>2</sub>O<sub>2</sub>S occurred for the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-A because larger specific surface area does not only increase the adsorption of CS<sub>2</sub>, but also supply a large interface. This interface accelerates the solid-gas reaction rate. For Yb<sub>2</sub>O<sub>3</sub>-B and Yb<sub>2</sub>O<sub>3</sub>-C, Yb<sub>2</sub>O<sub>2</sub>S faded at 800 °C and the formation of Yb<sub>2</sub>S<sub>3</sub> was similar.



Figure 2.4 Temperature dependences of diffraction intensity of reaction product formed via the sulfurization of  $Yb_2O_3$  for 1 hr or 3 hr with gas flow rate of 1.67 mL/s.
Figure 2.5 shows temperature dependences of diffraction intensity of Yb<sub>2</sub>O<sub>3</sub> (222), Yb<sub>2</sub>O<sub>2</sub>S (011),  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> (206) and  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> (110) formed via the sulfurization of Yb<sub>2</sub>O<sub>3</sub> at 500 °C ~ 1050 °C for 8 hr with GFR of 0.83 mL/s. For the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-A, single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> phase appeared at 600 °C, reached its maximum intensity at 950 °C and disappeared at 1000°C. Orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> phase was observed at 700°C for Yb<sub>2</sub>O<sub>3</sub>-B and Yb<sub>2</sub>O<sub>3</sub>-C powders, and the maximum of diffraction intensity of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> was detected at 850°C for Yb<sub>2</sub>O<sub>3</sub>-B and 800 °C for Yb<sub>2</sub>O<sub>3</sub>-C powders, respectively.

Different with the sulfurization process of  $Yb_2O_3$ -A,  $Yb_2O_2S$  phase emerged as intermediate product.  $Yb_2O_2S$  phase was observed at 700 °C for  $Yb_2O_3$ -B and  $Yb_2O_3$ -C. The corresponding maximum diffraction intensity of  $Yb_2O_2S$  was detected at 700°C, and disappeared at 800 °C for  $Yb_2O_3$ -B and 930°C for  $Yb_2O_3$ -C, respectively.

Hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> emerged at different temperature and enhanced gradually as the temperature increased. Single-phase  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> was confirmed at above 1000°C except for the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-D. For the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-D, Yb<sub>2</sub>O<sub>2</sub>S phase existed until 1050 °C for 8 hr.

The compositions of synthetics sulfurized for 8 hr were listed in Table 2.4. For  $Yb_2O_3$ -A, sulfurization product is single  $\eta$ - $Yb_2S_3$  at 600~ 850 °C (Figure 2.5) and its composition becomes equal to theoretical value of  $Yb_2S_3$ . The impurity content of  $Yb_2S_3$  formed by sulfurized  $Yb_2O_3$ -B at 930 °C for 8 hr increased to 0.78% but the impurity content reduced to 0.22% for the sulfurization of  $Yb_2O_3$ -C at same conditions.

The oxygen content and carbon content for  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> produced by sulfurized Yb<sub>2</sub>O<sub>3</sub>-C at 1050°C for 8 hr with GFR of 3.33 mL/s were 0.62% and 0.86%, respectively. When GFR lessened to 0.83 mL/s, the oxygen content and carbon content were 0.48% and 0.23%, respectively. It showed the impurity contents of Yb<sub>2</sub>S<sub>3</sub> powders are dependent on GFR. Therefore, purer samples can be made in proper GFR and sulfurization temperature to void the decomposition of excess CS<sub>2</sub> gas.



Figure 2.5 Temperature dependences of diffraction intensity of reaction products formed the sulfurization of  $Yb_2O_3$  for 8 hr with gas flow rate of 0.83 mL/s.

Starting materials	Condition		Product	Composition (mass %)		
	°C	mL/s	1100000	Yb	S	Impurity
Yb <sub>2</sub> O <sub>3</sub> -A	850	0.83	$\eta$ -Yb <sub>2</sub> S <sub>3</sub>	78.07	21.66	0.27
Yb <sub>2</sub> O <sub>3</sub> -B	930	0.83	$M-Yb_2S_3$	78.88	20.34	0.78
Yb <sub>2</sub> O <sub>3</sub> -C	850	0.83	$M-Yb_2S_3$	78.58	21.03	0.39
Yb <sub>2</sub> O <sub>3</sub> -C	930	0.83	$M-Yb_2S_3$	78.11	21.67	0.22
Yb <sub>2</sub> O <sub>3</sub> -C	1050	0.83	ε-Yb <sub>2</sub> S <sub>3</sub>	78.0	21.7	0.71
Yb <sub>2</sub> O <sub>3</sub> -C	1050	3.33	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	77.5	21.4	1.48

Table 2.4 Chemical composition of Yb<sub>2</sub>S<sub>3</sub> sulfurized for 8 hr

Theory value  $W_{Yb}$ = 78.28%; Ws= 21.72%; M-Yb<sub>2</sub>S<sub>3</sub>: mixture of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub>.

2.3.3 Morphology, particle size distribution and specific surface area of Yb<sub>2</sub>S<sub>3</sub>

Figure 2.6 shows typical SEM micrographs of Yb<sub>2</sub>S<sub>3</sub> formed by the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-A powders. The shape of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> produced at 700°C for 1 hr with GFR of 1.67 mL/s (Figure 2.6a) is similar with that of Yb<sub>2</sub>O<sub>3</sub>-A (Figure 2.1a). Following sulfurization temperature increased to 1000 °C,  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> phase transformed to  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase (Figure 2.6b).



Figure 2.6 SEM micrographs of  $Yb_2S_3$  by sulfurized  $Yb_2O_3$ -A at 700°C (a) and 1000°C (b) for 1hr with gas flow rate of 1.67 mL/s.

Figure 2.7 shows SEM micrographs of Yb<sub>2</sub>S<sub>3</sub> prepared by the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-B at 800 ~ 1050 °C for 1 hr with GFR of 1.67 mL/s. Figure 2.7a shows the partial agglutination of single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> phase. In Figure 2.7b, the sulfurization product has larger particle size than that of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> in Figure 2.7a, implying that  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> particle grows as the temperature increases to 900 °C. From 900 °C to 1000°C, residual  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> (mass fraction 24%) transformed to single  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub>, which was accelerated by increase of impurity content (Table 2.3), just like the effecting of carbon on the sintered La<sub>2</sub>S<sub>3</sub> powders[81]. The important point to note is particle size of single  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> reduces after sulfurization at 1050°C.



Figure 2.7 SEM micrographs of Yb<sub>2</sub>S<sub>3</sub> formed by the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-B at 800°C (a), 900°C (b), 1000 °C (c) and 1050 °C (d) for 1hr with gas flow rate of 1.67 mL/s.

Figure 2.8 shows SEM micrographs of Yb<sub>2</sub>S<sub>3</sub> produced by the sulfurization of Yb<sub>2</sub>O<sub>3</sub>-C powders with GFR of 1.67 mL/s. In Figure 2.8a and 2.8b, particle size of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> is bigger than that of primary Yb<sub>2</sub>O<sub>3</sub>-C particles (Figure 2.1c). It is mainly due to sulfur atom having a bigger diameter than oxygen atom. During the sulfurization process, oxygen atoms in sites of Yb<sub>2</sub>O<sub>3</sub> lattice are replaced by sulfur atoms and the density lessens from 9.22 g/cm<sup>-3</sup> of Yb<sub>2</sub>O<sub>3</sub> to 6.02 g/cm<sup>-3</sup> of Yb<sub>2</sub>S<sub>3</sub>. On the other hand, the agglomeration of Yb<sub>2</sub>S<sub>3</sub> produces rounded balls with different size, which did not occurred during sulfurization processes of other Yb<sub>2</sub>O<sub>3</sub>. The formation

of Yb<sub>2</sub>S<sub>3</sub> rounded balls can be explained by three aspects: 1) homogeneous spherical Yb<sub>2</sub>O<sub>3</sub>-C particles were sulfurized with same reaction rate; 2) spherical Yb<sub>2</sub>S<sub>3</sub> particle clustered together to lessen surface free energy; 3) volume shrinkage of phase transformation of Yb<sub>2</sub>S<sub>3</sub> accelerated the formation of Yb<sub>2</sub>S<sub>3</sub> ball. Figure 2.8c and Figure 2.8d show morphology of  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase. The average particle size of  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> balls (top right of Figure 2.8d) is lower than that of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> balls (top right of Figure 2.8a).



Figure 2.8 SEM micrographs of  $Yb_2S_3$  formed by the sulfurization of  $Yb_2O_3$ -C at 800°C (a), 900°C (b), 1000 °C (c) and 1050 °C (d) for 1 hr with gas flow rate of 1.67 mL/s.

Figure 2.9 shows typical SEM micrographs of synthetic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> powders by sulfurized Yb<sub>2</sub>O<sub>3</sub>-A at 650 °C (a), 750 °C (b) and at 850 °C (c) for 8 hr with flow rate of 0.83 mL/s. Figure 2.9a, the shape of synthetic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> is similar with that of Yb<sub>2</sub>O<sub>3</sub>-A. The particle size of Yb<sub>2</sub>S<sub>3</sub> is bigger than that of Yb<sub>2</sub>O<sub>3</sub> due to sulfur having a bigger diameter than oxygen. During the sulfurization process, the sites of oxygen in Yb<sub>2</sub>O<sub>3</sub> lattice are replaced by sulfur, the grain grows, and the density decrease from 9.22 g/cm<sup>-3</sup> of oxide to 6.17 g/cm<sup>-3</sup> of sesquisulfide.



Figure 2.9 SEM images of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> by sulfurized Yb<sub>2</sub>O<sub>3</sub>-A at 650 °C (a), 750 °C (b) and 850 °C (c) for 8 hr with flow rate of 0.83 mL/s.

Figure 2.10 shows particle size distribution of synthetic orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> sulfurized at 800 °C and hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> sulfurized at 1000 °C. In Figure 2.10a, the average particle size of orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> is 5.27µm for Yb<sub>2</sub>O<sub>3</sub>-A, 11.83 µm for Yb<sub>2</sub>O<sub>3</sub>-B and 41.24 µm for Yb<sub>2</sub>O<sub>3</sub>-C. However, average particle size of hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> (Figure 2.10b) is 3.71µm for Yb<sub>2</sub>O<sub>3</sub>-A, 10.00 µm for Yb<sub>2</sub>O<sub>3</sub>-B and 40.77 µm for Yb<sub>2</sub>O<sub>3</sub>-C, which is smaller than that of orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> because of the volume shrinkage of Yb<sub>2</sub>S<sub>3</sub> during phase transformation. Both orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> have larger particles than that of their oxides for three kinds of Yb<sub>2</sub>O<sub>3</sub>.



Figure 2.10 Particle size distributions of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> (a) sulfurized at 800 °C and  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> (b) sulfurized at 1000 °C

Figure 2.11 shows SSA results of Yb<sub>2</sub>S<sub>3</sub> formed by sulfurized Yb<sub>2</sub>O<sub>3</sub>-A~C at 700 ~ 1050°C for 1 hr with CS<sub>2</sub> gas flow rate of 1.67 mL/s. For Yb<sub>2</sub>O<sub>3</sub>-A, SSA of single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> lessened as temperature increased to 900 °C, which is attributed to the growth of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> crystals. According to Figure 2.3a, the transformation of orthorhombic-to-hexagonal Yb<sub>2</sub>S<sub>3</sub> phase was accelerated from 1000°C to 1050°C. The volume shrinkage of Yb<sub>2</sub>S<sub>3</sub> during phase transformation leaded to the addition of SSA value.

SSA of Yb<sub>2</sub>S<sub>3</sub> formed by sulfurized Yb<sub>2</sub>O<sub>3</sub>-B decreases to minimum and then rose with temperature. This variation implies particle size of Yb<sub>2</sub>S<sub>3</sub> increases and then decreases from 800 °C to 1050 °C, which is consistent with SEM micrographs of Yb<sub>2</sub>S<sub>3</sub> as shown in Figure 2.7. For Yb<sub>2</sub>O<sub>3</sub>-C, SSA of Yb<sub>2</sub>S<sub>3</sub> reduces from 800 °C to 900 °C, which is similar with those of Yb<sub>2</sub>O<sub>3</sub>-A and Yb<sub>2</sub>O<sub>3</sub>-B. According to SEM results in Figure 2.8, the average particle size of  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> is smaller than that of  $\eta$ -Yb<sub>2</sub>S<sub>3</sub>, so SSA of  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> increases at 1000 °C.



Figure 2.11 Specific surface area of  $Yb_2S_3$  from  $Yb_2O_3$ -A ~C sulfurized at 700 ~ 1000 °C for 1 hr with gas flow rate of 1.67 mL/s.

2.3.4 Kinetic analysis of reaction rate

The sulfurization reaction mainly depends on three elements: 1) whether  $CS_2$  gas adsorption is above the critical value for the diffusion through the boundary layer; 2) the formation and diffusion of an interface of Yb<sub>2</sub>O<sub>2</sub>S or Yb<sub>2</sub>S<sub>3</sub>; 3) discharge rate of generated CO<sub>2</sub> gas. The reaction proceeds as follows:

$$2Yb_{2}O_{3}(s) + CS_{2}(g) \to 2Yb_{2}O_{2}S(s) + CO_{2}(g)$$
(1)

 $Yb_2O_2S(s) + CS_2(g) \rightarrow Yb_2S_3(s) + CO_2(g)$  (2)

The effect of GFR is dependent on SSA of Yb<sub>2</sub>O<sub>3</sub>. When GFR becomes 0.83 mL/s, larger SSA of Yb<sub>2</sub>O<sub>3</sub>-A supplies more chance for CS<sub>2</sub> molecules to adsorb on the surface of Yb<sub>2</sub>O<sub>3</sub> particle (Figure 2.1), which can promote the gas-solid reaction occurrence. It is the reason single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> can be prepared at relative low sulfurization temperature of 600 °C (Figure 2.3).

Following SSA of Yb<sub>2</sub>O<sub>3</sub>-B powders reduced to  $10\sim25 \text{ m}^2/\text{g}$ , the interplay of Yb<sub>2</sub>O<sub>3</sub>-B particle leads CS<sub>2</sub> adsorption capacity receded. Yb<sub>2</sub>O<sub>3</sub>-C powders have similar SSA and particle size with Yb<sub>2</sub>O<sub>3</sub>-B, so sulfurization products are similar in Figure 2.3c and Figure 2.4. Therefore, single  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> cannot be obtained from Yb<sub>2</sub>O<sub>3</sub>-B~D at 600°C ~ 800°C with GFR of 0.83 mL/s (Figure 2.4). If GFR is 1.67 mL/s, enough CS<sub>2</sub> molecules adsorb on the surface of every Yb<sub>2</sub>O<sub>3</sub> particle and the sulfurization reaction can be completed. So there is no Yb<sub>2</sub>O<sub>2</sub>S in Figure 2.3b and

Figure 2.3c.

Particle size of Yb<sub>2</sub>O<sub>3</sub> is the main affecting factor for the formation and diffusion of the interface of Yb<sub>2</sub>O<sub>2</sub>S or Yb<sub>2</sub>S<sub>3</sub>. According to SEM results in Figure 2.1, the diffusion of this interface can be quickly completed for Yb<sub>2</sub>O<sub>3</sub>-B and Yb<sub>2</sub>O<sub>3</sub>-C because particle size of Yb<sub>2</sub>O<sub>3</sub>-B or Yb<sub>2</sub>O<sub>3</sub>-C is smaller than that of Yb<sub>2</sub>O<sub>3</sub>-A, so single  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> phase can be prepared by the shorter time of 1 hr at 1000 °C or 0.5 hr at 1050 °C (Figure 2.3). Moreover, sphere Yb<sub>2</sub>O<sub>3</sub>-C particles are easy to bond together and produce Yb<sub>2</sub>S<sub>3</sub> balls (Figure 2.7).

For Yb<sub>2</sub>O<sub>3</sub>-D, the existence of Yb<sub>2</sub>O<sub>2</sub>S can be explained in three aspects: 1) SSA of Yb<sub>2</sub>O<sub>3</sub>-D is too small to absorb enough CS<sub>2</sub> molecules with GFR of 1.67 mL/s; 2) particle size of Yb<sub>2</sub>O<sub>3</sub>-D is too large to finish sulfurization process completely; 3) the diffusion of generated CO<sub>2</sub> from inner to outside was bated at a certain degree. Hence, the inner of Yb<sub>2</sub>O<sub>3</sub> particle is difficult to be sulfurized to Yb<sub>2</sub>S<sub>3</sub> but turned to Yb<sub>2</sub>O<sub>2</sub>S at above 1000°C (Figure 2.2d and Figure 2.4).

Compared with the sulfurization processes of four sets of recipes, small particle size and large SSA are necessary for preparation of single  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> and appropriate GFR (1.67 mL/s) can accelerate the sulfurization reaction. Bigger specific surface area lessens the sulfurization temperature to 600 °C due to enhancement of CS<sub>2</sub> adsorbing capacity on the surface of every Yb<sub>2</sub>O<sub>3</sub>-A particle.

2.3.5 Comparison of synthesis process of rare-earth sesquisulfides

Table 2.5 shows the particle sizes of starting materials and minimum sulfurization temperature required for single  $Ln_2S_3$  phase. In addition, the oxygen and carbon contents of  $Ln_2S_3$  obtained under the abovementioned conditions and intermediate products are listed. Generally speaking, the sulfurization temperature is higher for heavy  $Ln_2S_3$  than that of light  $Ln_2S_3$ . For light rare earths, whether particle size of  $Ln_2O_3$  is small (1.8 µm of  $La_2O_3$ ) or large (16 µm of  $Nd_2O_3$ ), single  $Ln_2S_3$  phase can be prepared. Nevertheless, the products from heavy  $Ln_2O_3$  contain oxysulfide residues when particle size of heavy  $Ln_2O_3$  is large (5 µm of  $Yb_2O_3$  and 6.5 µm of  $Lu_2O_3$ ). Therefore, heavy  $Ln_2O_3$  are comparatively difficult to be sulfurized than light  $Ln_2O_3$ .

In this study, sulfurization temperature of heavy Yb<sub>2</sub>O<sub>3</sub> was lessened to 600 °C for  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and 1000 °C for  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> by varying the characters of starting material Yb<sub>2</sub>O<sub>3</sub>. This discovery is not only for preparation of single Yb<sub>2</sub>S<sub>3</sub> but also for fabrication of

all  $Ln_2S_3$  at lower temperature with small particle size and large specific surface area of  $Ln_2O_3$  as starting material.

Starting	Dortiala	Sulfurization						
Starting	raticle	Temp.	Final	Intermediate	Oxygen	Carbon	Deference	
material	size/µm	∕°C	Products	Products	/mass%	/mass%	Reference	
La <sub>2</sub> O <sub>3</sub>	1.8	750	$\beta$ -La <sub>2</sub> S <sub>3</sub>	$La_2O_2S$ ,	0.91	0.02	Ref. 8	
CeO <sub>2</sub>	4.3	700	$\alpha$ -Ce <sub>2</sub> S <sub>3</sub>	$Ce_2O_2S$ , $CeS_2$	1.30	0.10	Ref. 9	
Pr <sub>6</sub> O <sub>11</sub>	7.5	850	$\beta$ -Pr <sub>2</sub> S <sub>3</sub>	$\begin{array}{c} Pr_2O_2S,\\ \alpha-Pr_2S_3, \end{array}$	0.45	0.06	Ref. 10	
Nd <sub>2</sub> O <sub>3</sub>	16	1000	$\beta$ -Nd <sub>2</sub> S <sub>3</sub>	$\begin{array}{c} Nd_2O_2S,\\ \alpha-Nd_2S_3, \end{array}$	0.25	0.32	Ref. 10	
$Sm_2O_3$	9.8	850	$\alpha$ -Sm <sub>2</sub> S <sub>3</sub>	$Sm_2O_2S$ ,	0.52	0.03	Ref. 8	
$Eu_2O_3$	3.5	800	EuS	$EuS_2$ , $Eu_3S_4$	0.52	0.05	—	
$Gd_2O_3$	1.0	975	$\alpha$ -Gd <sub>2</sub> S <sub>3</sub>	$Gd_2O_2S, GdS_2$	0.25	0.43	Ref. 11	
Tb <sub>4</sub> O <sub>7</sub>	3.0	1050	$\alpha$ -Tb <sub>2</sub> S <sub>3</sub>	Tb <sub>2</sub> O <sub>2</sub> S	0.41	0.14	Ref. 11	
Dy <sub>2</sub> O <sub>3</sub>	1.0	975	$\alpha$ -Dy <sub>2</sub> S <sub>3</sub>	Dy <sub>2</sub> O <sub>2</sub> S	-	-	—	
Ho <sub>2</sub> O <sub>3</sub>	1.6	1050	$\delta$ -Ho <sub>2</sub> S <sub>3</sub>	Ho <sub>2</sub> O <sub>2</sub> S	0.52	0.78	Ref. 12	
	0.4	1000	o Vh-S-	$Yb_2O_2S$ ,	0.62	0.86		
	0.4	1000	E-10253	$\eta$ -Yb <sub>2</sub> S <sub>3</sub>	(1050°C)	(1050°C)		
Vh <sub>2</sub> O <sub>2</sub>	1.0	700	$\eta$ -Yb <sub>2</sub> S <sub>3</sub>	_	-	-	_	
10203	1.0	1000	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	$\eta$ -Yb <sub>2</sub> S <sub>3</sub>	-	-		
	5	1050	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub> , Yb <sub>2</sub> O <sub>2</sub> S	Yb <sub>2</sub> O <sub>2</sub> S	Ι	Ι		
Lu <sub>2</sub> O <sub>3</sub>	6.5	1050	$\epsilon$ -Lu <sub>2</sub> S <sub>3</sub> , Lu <sub>2</sub> O <sub>2</sub> S	Lu <sub>2</sub> O <sub>2</sub> S	_	_	-	

Table 2.5 Particle size of starting material and minimum sulfurization temperature required for single Ln<sub>2</sub>S<sub>3</sub> phase (sulfurization time: 8 hr)

α: Orthorhombic (Gd<sub>2</sub>S<sub>3</sub> type), β: Tetragonal ( $Pr_{10}S_{14}O$  type), γ: Cubic (Th<sub>3</sub>P<sub>4</sub> type) δ: Monoclinic ( $Er_2S_3$  type), η: Orthorhombic ( $Sc_2S_3$  type), ε: Hexagonal

#### 2.4 Heat treatment and sintering of ytterbium sulfides

In this section, the formation behavior of  $Yb_2S_3$  synthesized via  $CS_2$  gas sulfurization of  $Yb_2O_3$  was investigated. Dependences of temperature on formation of  $Yb_2S_3$  were systematically researched. Influences of specific surface area and particle size of  $Yb_2O_3$  on the sulfurization process were discussed. Furthermore, it is meaningful to prepare  $Yb_3S_4$  or YbS by heat treatment of  $Yb_2S_3$  under different atmospheres.

2.4.1 Heat treatment of Yb<sub>2</sub>S<sub>3</sub> under Ar or Ar/CS<sub>2</sub> gas

The synthetic  $Yb_2S_3$  powders were heat treated under different conditions to synthesize  $Yb_3S_4$  phase. XRD patterns of the synthetic from treated  $Yb_2S_3$  powders are shown in Fig. 12. In Fig. 12, each of the  $Yb_2S_3$  powders underwent orthorhombic-to-hexagonal phase transition upon heat treatment at 1000 °C for 3 hr in  $Ar/CS_2$  atmosphere. However, XRD results showed that orthorhombic  $Yb_3S_4$  was main phase after heat treatment at 1050°C for 8 hr under Ar atmosphere and  $Yb_2S_3$  nearly disappeared upon prolonged (12 hr) heat treatment.

Table 2.6 shows chemical compositions of synthetics by treated Yb<sub>2</sub>S<sub>3</sub> powders under Ar gas for 5 ~ 12 hr. There is phase transformation of synthetic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> powders with orthorhombic structure to hexagonal structure at 1000°C for 5 hr or 6 hr. Compared with starting material Yb<sub>2</sub>O<sub>3</sub>-A, the composition of synthetic  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> by heat treatment is more approximate to theory value of Yb<sub>2</sub>S<sub>3</sub> (Yb theory content 78.28%, S theory content 21.72%). And then, the impurity content is least for raw material Yb<sub>2</sub>O<sub>3</sub>-C. For longer heat-treatment time (6 hr), the product  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> has no change but the content of sulfur is lower than that of sample treated 5 hr, which imply the mechanism of phase change is possibly sulfur lost during heat-treatment. If the treatment temperature is added to 1050 °C or time is lengthened to 8 hr or 12 hr, Yb<sub>3</sub>S<sub>4</sub> is able to obtain. However, it is also connected with sulfurization procedure and impurity contents. In the other words, the residual carbon content will influence the stability of Yb<sub>2</sub>S<sub>3</sub>. Although the phase transformation from  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> to Yb<sub>3</sub>S<sub>4</sub> has some differences with their theory values.

Table 2.6 Chemical composition of synthetics by treated Yb<sub>2</sub>S<sub>3</sub> powders under Ar gas

Raw	Sulfuriza	ation	Heat-treat		Draduat	Composition (%)		
Yb <sub>2</sub> O <sub>3</sub>	°C	hr	°C	ks	Product	Yb	S	Impurity
Yb <sub>2</sub> O <sub>3</sub> -A	800	3	1000	5	ε-Yb <sub>2</sub> S <sub>3</sub>	78.62	20.9	0.45
Yb <sub>2</sub> O <sub>3</sub> -B	800	3	1000	5	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.1	21.7	0.19
Yb <sub>2</sub> O <sub>3</sub> -C	800	3	1000	5	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.2	21.7	0.09
Yb <sub>2</sub> O <sub>3</sub> -B	800	4	1000	6	$\epsilon$ -Yb <sub>2</sub> S <sub>3</sub>	78.8	20.5	0.7
Yb <sub>2</sub> O <sub>3</sub> -B	930	4	1050	8	Yb <sub>3</sub> S <sub>4</sub>	79.1	19.5	1.3
Yb <sub>2</sub> O <sub>3</sub> -B	800	4	1050	12	Yb <sub>3</sub> S <sub>4</sub>	78.6	19.4	2.0
Yb <sub>2</sub> O <sub>3</sub> -C	800	4	1050	12	$Yb_3S_4$	78.0	19.2	2.7
Yb <sub>2</sub> O <sub>3</sub> -B	1050	8	1050	12	Yb <sub>3</sub> S <sub>4</sub>	79.1	19.5	1.44

for  $5 \sim 12$  hr



Fig. 2.12 XRD patterns of heat-treatment products under normal pressure 2.4.2 Heat treatment of  $Yb_2S_3$  under vacuum

Figure 2.13 showed representative XRD patterns for the reaction products annealed synthetic Yb<sub>2</sub>S<sub>3</sub> powders at 1000 °C ~ 1500 °C for 1 hr ~ 5 hr. Under the annealing temperature of 1000°C, hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> has no variation for 1 hr. Following time increased to 3 hr, hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> has completely transformed to Yb<sub>3</sub>S<sub>4</sub>. At 1200 °C, diffraction peaks of YbS were observed for 5 hr. The intensity of diffraction peaks of Yb<sub>3</sub>S<sub>4</sub> reduced following annealing temperature increased to 1500 °C. Single YbS having a homogeneity range YbS<sub>1.11-1.15</sub> was formed at 1500 °C for 3 hr.



Fig. 2.13 XRD patterns of heat-treatment products under vacuum XRD patterns for the reaction products sintered at 1000 ~ 1400 °C by SPS are shown in Fig. 2.14. At 1000 °C and 1100 °C, the diffraction peaks of hexagonal ε-Yb<sub>2</sub>S<sub>3</sub> had no change. As the sintering temperature enlarged to about 1300 °C, the slight diffraction peaks of orthorhombic Yb<sub>3</sub>S<sub>4</sub> were observed. It displays that hexagonal ε-Yb<sub>2</sub>S<sub>3</sub> transform to Yb<sub>3</sub>S<sub>4</sub> on the surface of compact at high sintering temperature. However, this transformation of Yb<sub>2</sub>S<sub>3</sub> to Yb<sub>3</sub>S<sub>4</sub> was inhabited under closed carbon mold.



Fig. 2.14 XRD patterns of heat-treatment products by SPS Base on the above-mentioned annealing results, ytterbium monosulfide can be formed by annealing the sesquisulfide at high temperature. Ytterbium are easier to be reduced to the divalent state than the others lanthanide element due to their full 4f shell electronic structures.

## 2.5 Sintering and Heat capacity of Yb<sub>3</sub>S<sub>4</sub> and YbS

Figure 2.15 showed XRD patterns of Yb<sub>3</sub>S<sub>4</sub> and YbS compacts sintered from the annealed Yb<sub>3</sub>S<sub>4</sub> and YbS powder at 1550 °C for 1 or 3 hr and 1600 °C for 0.33 hr, respectively. XRD results suggested that Yb<sub>3</sub>S<sub>4</sub> was stable at about 1550 °C. Yb<sub>3</sub>S<sub>4</sub> is difficult to transform and decompose to YbS during SPS sintering. YbS bulk was easy to be broken during sintering process due to its NaCl structure.



Fig. 2.15 XRD patterns of  $Yb_3S_4$  and YbS compacts sintered from the annealed  $Yb_3S_4$  and YbS powder

Figure 2.16 shows SEM micrographs analysis of sintered  $Yb_3S_4$  and YbS compacts from the annealed  $Yb_3S_4$  and YbS powder. In Fig. 2.17, there are local microcracks in synthetic  $Yb_3S_4$ , which is the reason for the sample broken. On the other hand, both  $Yb_3S_4$  and YbS compacts have some poles, which may be caused by the high temperature sulfur loss.



Fig. 2.16 SEM micrographs of Yb<sub>3</sub>S<sub>4</sub> and YbS compacts sintered from the annealed Yb<sub>3</sub>S<sub>4</sub> at 1500 °C for 5h and YbS powder at 1600 °C for 0.33 hr

Figure 2.17 shows the temperature dependence of specific heats for Yb<sub>3</sub>S<sub>4</sub> and YbS compacts sintered from the annealed Yb<sub>3</sub>S<sub>4</sub> at 1500 °C for 5h and YbS powder at 1600 °C for 0.33 hr. A broad peak appears at about 4 K for Yb<sub>3</sub>S<sub>4</sub> with a peak value of 5.1 J/K·mol<sup>-1</sup>, which is smaller than that former research result of Yb<sub>3</sub>S<sub>4</sub> (5.5 J/K·mol<sup>-1</sup> at 4.3 K). Moreover, the peak value per Yb<sup>3+</sup> is evaluated as 1.46 J/K Yb<sup>3+</sup>, which included the contributions of the crystal field and phonon. This value seems to be smaller than that of calculated with the S=1/2 impurity Kondo model. And then, there is no peak for antiferromagnetic YbS.



Fig. 2.17 heat capacity of Yb<sub>3</sub>S<sub>4</sub> and YbS compacts sintered from the annealed Yb<sub>3</sub>S<sub>4</sub> at 1500 °C for 5h and YbS powder at 1600 °C for 0.33 hr

### **2.6 Conclusions**

In the synthesis of ytterbium sulfides, a new polymorphic form of Yb<sub>2</sub>S<sub>3</sub> with an orthorhombic structure has been observed and obtained at 600 ~ 850 °C, single-phase  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> was prepared above 1000 °C for 8 hr. In the annealing of synthetic  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub>, Yb<sub>3</sub>S<sub>4</sub> and YbS could be formed by decomposed Yb<sub>2</sub>S<sub>3</sub> at high temperature. On the other hand, bigger specific surface area can reduce the sulfurization temperature and accelerate the sulfurization reaction. The impurity contents of oxygen and carbon in synthetic powders and the particle size of synthetic powders were dependent on the sulfurization conditions, especially the CS<sub>2</sub> gas flow rate.

Yb<sub>2</sub>O<sub>3</sub> powders with different characters were employed to research the influence of particle size and specific surface area on the synthesis of Yb<sub>2</sub>S<sub>3</sub>. The main conclusions are as follows: (1) High sulfurization temperature (1000 °C) and small particle size are necessary for preparation of single hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub>. Larger specific surface area (50 m<sup>2</sup>/g) of Yb<sub>2</sub>O<sub>3</sub> is better for fabrication of orthorhombic

 $\eta$ -Yb<sub>2</sub>S<sub>3</sub> at low temperature of 600 °C for 8 hr. However, single Yb<sub>2</sub>S<sub>3</sub> cannot be obtained if specific surface area of Yb<sub>2</sub>O<sub>3</sub> is less than 2 m<sup>2</sup>/g and particle size is larger than 5  $\mu$ m. (2) Sulfurization time (0.5 hr) tends to decrease with increasing temperature (1050 °C). CS<sub>2</sub> gas flow rate does not only influence the sulfurization efficiency and products, but also control the impurity content. Particle sizes of synthetic orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> are dependent on sulfurization condition and impurity content. (3) Heavy Ln<sub>2</sub>O<sub>3</sub> are comparatively difficult to be sulfurized than light Ln<sub>2</sub>O<sub>3</sub>. To modify characters of Ln<sub>2</sub>O<sub>3</sub> is an effective step for preparation of Ln<sub>2</sub>S<sub>3</sub>.

Hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> was synthesized at above 1000°C by sulfurizing its oxide with CS<sub>2</sub> gas. The synthetic Yb<sub>2</sub>S<sub>3</sub> is more stable in sulfur-rich atmosphere than argon gas or vacuum at about 1000°C. Yb<sub>2</sub>S<sub>3</sub> phase transformed to Yb<sub>3</sub>S<sub>4</sub> phase (1000 °C for 3 hr or 1200 °C for 1 hr) or YbS phase (1500 °C for 3 hr) during annealing. Yb<sub>2</sub>S<sub>3</sub> had better phase stability below 1400 °C with spark plasma sintering. The phase stability of Yb<sub>2</sub>S<sub>3</sub> probably depended on the sulfur vapor pressure. Yb<sub>3</sub>S<sub>4</sub> and YbS were sintered by spark plasmas sintering at 1500 °C for 5 hr and 1600 °C for 0.33 hr, respectively. The heat capacity of synthetic Yb<sub>3</sub>S<sub>4</sub> and YbS was measured at 2- 50 K and compared with previous reported.

# Chapter 3 Preparation, sintering and large magnetocaloric effect of europium sulfides

### **3.1 Introduction**

Europium is one of the unusual rare earth elements, because in solids it occurs in different valence states: it can be either divalent, trivalent or of mixed valency[94]. Bivalent europium (with 7 electrons in the 4f orbital) and trivalent europium (having 6 electrons in the 4f orbital) are the two main oxidation states of europium. The valence of europium is strongly dependent on temperature and valence change can cause phase transformation of Eu<sub>3</sub>S<sub>4</sub>-to-EuS.

There are three main europium sulfide species, i.e., EuS, Eu<sub>3</sub>S<sub>4</sub>, and EuS<sub>2</sub> [95]. Recently, there has been important attention in EuS nanoparticles as prospective optomagnetic and luminescent materials because the crystal size of these particles affects the optomagnetic and luminescent properties [96]. EuS has received considerable attention because of its unique photophysical and magnetooptical properties [97] and exhibits spin-filtering effects with potential application in spintronics [98]. EuS is an important starting material for the Eu-Cu-S system [99], the Eu-R-S system (R = La, Ce, Pr, Nd, and Gd) [100], and the Eu-Pb-S system [101, 102]. Partial Eu-substitution of the fluorescent sulfide material BaAl<sub>2</sub>S<sub>4</sub> synthesized from the mixture of Al<sub>2</sub>S<sub>3</sub>, BaS, and EuS, is anticipated to be applicable for development of an inorganic electroluminescence (EL) display [97].

Single crystal EuS has a large magnetocaloric effect  $(37 \text{ J} \cdot \text{Kg}^{-1} \cdot \text{K}^{-1})$  at 18.5 K near the liquid hydrogen temperature of 20 K [103]. For storage and transportation of hydrogen fuel, it is effective to liquefy hydrogen; therefore, a regenerating agent with a large magnetocaloric effect near the liquid hydrogen temperature is required [104].

Mixed valence Eu<sub>3</sub>S<sub>4</sub> with the formula of  $(Eu^{2+})(Eu^{3+})_2S_4$  is sensitive to temperature. Eu<sub>3</sub>S<sub>4</sub> crystals can act as sites for nucleation to accelerate the formation of  $\gamma$ -La<sub>2</sub>S<sub>3</sub> during the nucleation process, which is advantageous for the preparation and stabilization of  $\gamma$ -La<sub>2</sub>S<sub>3</sub> at low-temperature[9]. EuLn<sub>2</sub>S<sub>4</sub> (Ln = La-Gd) with Th<sub>3</sub>P<sub>4</sub> structure is a rare p-type semiconductor with a relatively large Seebeck coefficient of 350  $\mu$ V·K<sup>-1</sup> at around 340 K[100].

Traditionally, EuS powders are generally prepared from the constituents [95] or

by CS<sub>2</sub>-gas [105] or H<sub>2</sub>S-gas sulfurization [106] of Eu<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>S-gas sulfurization process of Eu<sub>2</sub>O<sub>3</sub> conducted over several days and high sulfurization temperature (1523 K) is necessary for the minimum oxygen concentration in the synthetic EuS [106]. Compared with H<sub>2</sub>S sulfurization, CS<sub>2</sub> gas is a more effective sulfurization agent, which have been proven during the preparation of binary rare-earth sesquisulfides from their oxides [6]. These sesquisulfides can be obtained at a lower temperature by CS<sub>2</sub>-gas sulfurization than that of H<sub>2</sub>S-gas sulfurization, as is evident from the change in the standard free energy of formation of sulfurization.

The most common method for the synthesis of EuS nanoparticle is thermal decomposition of dithiocarbamate complexes in coordinating solvents [107]. EuS nanocrystals with narrow size distribution are synthesized in high yields by the thermal decomposition of  $Eu(oleate)_3$  in oleylamine using  $CS_2$  as the sulfur source[108]. To overcome the problem of yield and purity for thermal decomposition method,  $Eu_2O_3$  nanowires were employed to synthesize EuS via H<sub>2</sub>S-gas sulfurization [109, 110]. However, there is no report about  $CS_2$ -gas sulfurization of nanoscale  $Eu_2O_3$  with different shapes for the preparation of EuS.

In the Chapter 2, the formation of sesquisulfide was found to be dependent on the particle size and specific surface area of Yb<sub>2</sub>O<sub>3</sub> used as the starting material[111]. In general, the sulfurization of Yb<sub>2</sub>O<sub>3</sub> results in the formation of hexagonal Yb<sub>2</sub>S<sub>3</sub> through Yb<sub>2</sub>O<sub>2</sub>S. When Yb<sub>2</sub>O<sub>3</sub> with a particle size below 1  $\mu$ m and a specific surface area of 50 m<sup>2</sup>/g was employed, a new polymorphic Yb<sub>2</sub>S<sub>3</sub> phase with an orthorhombic structure was obtained at 873 K [111]. Europium is similar with ytterbium on the stable divalence and half-filled 4f electric structure, so it is meaningful to study the influences of particle size and SSA of Eu<sub>2</sub>O<sub>3</sub> on sulfurization process.

In this chapter, the formation of europium sulfides, especially  $Eu_3S_4$  and EuS, is investigated via  $CS_2$ -gas sulfurization of three kinds of nanoscale  $Eu_2O_3$  powders with different characteristics. The dependence of the sulfurization products on the conditions and the initially synthesized powder is systematically evaluated. Morphology and SSA of synthetics were characterized by high resolution scanning electron microscopy (SEM) and the Multi-point Brunauer, Emmett and Teller (BET) method. Sulfurization reaction processes were analyzed with thermodynamic calculation. We also examine the optimal heat-treatment conditions for synthetic EuS based on X-ray diffraction analysis by subjecting the obtained europium sulfides to heat treatment in different atmospheres. Polycrystalline materials that can be manufactured into plate, sphere or both are necessary for practical use of magnetic materials in magnetic refrigerator. Moreover, MCE of polycrystalline EuS is required to have similar value to that of a single crystal. Magnetocaloric effect of EuS sintered at 1000 °C and 1600 °C from two kinds of Eu<sub>2</sub>O<sub>3</sub> was investigated.

### **3.2 Experimental procedure**

Herein, Eu<sub>2</sub>O<sub>3</sub> powders (SSA of 9.33 m<sup>2</sup>/g, purity of 99.99% mass fraction, average particle size ~100 nm, Shin-Etsu Chemical Co., Ltd., remarked as Eu<sub>2</sub>O<sub>3</sub>-A; SSA of 8.47 m<sup>2</sup>/g, purity of 99.9% mass fraction, mean particle size ~130 nm, Anan Kasei Co., Ltd. remarked as Eu<sub>2</sub>O<sub>3</sub>-B; particle distribution of nanowire Eu<sub>2</sub>O<sub>3</sub> ~ 2.5  $\mu$ m\*50 nm, remarked as Eu<sub>2</sub>O<sub>3</sub>-C) were examined as listed in Table 3.1. The CS<sub>2</sub> gas sulfurization process was described in our previous report [111]. The sulfurization condition is from 300 °C to 1050 °C for 0.5-8 hr with gas flowing rate (denoted as GFR) of 50-100 mL/min.

X-ray diffraction (XRD, Model Rint-Ultima+, Rigaku Corp., Tokyo, Japan) with monochromatic Cu-K $\alpha$  radiation at 40 kV and 20 mA was used to identify the synthesized products. The lattice parameters of the products were also calculated from the data acquired with a scan step of  $1.0 \times 10^{-3}$  degree for 2 s. The reaction degree was estimated from the relative intensities of the diffraction lines of each synthesized product. The oxygen and carbon content of the synthesized products were determined by oxygen analyzer (Model TC-436, Leco Corp., St. Joseph, MI) and carbon analyzer (Model CS-444LS, Leco Corp., St. Joseph, MI), respectively. The actual stoichiometry of the obtained products was estimated by oxidizing them to stoichiometric Eu<sub>2</sub>O<sub>3</sub> at 1000 °C. The sulfur content was calculated from the weight of Eu<sub>2</sub>O<sub>3</sub> and the mass change caused by the complete oxidation of the sulfide to the oxide.

The morphology of synthesized powders was characterized by SEM (JSM-5310LV, JEOL Ltd., Tokyo, Japan). The SSA of the synthetic products was measured by using a surface area and pore size analyzer (Autosorb-1, Quantachrome Instruments, Florida, USA) with  $N_2$  adsorption. The isothermal magnetization curves for sintered EuS compact were measured at 10 -30 K with a Quantum Design SQUID

magnetometer to check the magnetocaloric effect of polycrystalline EuS.

Heat treatment of the synthesized Eu<sub>3</sub>S<sub>4</sub> powders was performed under different conditions as follows: 1) Eu<sub>3</sub>S<sub>4</sub> powder was held at 673–1073 K for 1 hr under Ar/CS<sub>2</sub> or Ar gas. 2) Eu<sub>3</sub>S<sub>4</sub> powder was placed on a BN boat (inner diameter: 15 mm) and held at 773–1773 K for 1 hr under vacuum at less than  $1.4 \times 10^{-3}$  Pa.

Raw material	$SSA(m^2/g)$	Grain size	Purity (%)	Producer
Eu <sub>2</sub> O <sub>3</sub> -A	9.33	~100 nm	99.99	Shin-Etsu Chemical Co., Ltd.,
Eu <sub>2</sub> O <sub>3</sub> -B	8.47	~130 nm	99.9	Anan Kasei Co., Ltd.
Eu <sub>2</sub> O <sub>3</sub> -C	9.99	$\sim 2.5 \ \mu m^* 50 \ nm$	_	Preparation in our lab

Table 3.1 Information of Eu<sub>2</sub>O<sub>3</sub> powders with different characteristic

# **3.3 Influence of Eu<sub>2</sub>O<sub>3</sub> character and sulfurization conditions on the preparation of EuS**

3.3.1 Preparation of Eu<sub>3</sub>S<sub>4</sub> and EuS by CS<sub>2</sub>-gas sulfurization of Eu<sub>2</sub>O<sub>3</sub>

Figure 3.1 shows TEM images of the Eu<sub>2</sub>O<sub>3</sub> powder employed in this study. Eu<sub>2</sub>O<sub>3</sub>-A nanospheres have a uniform size of ~100 nm and SSA is 9.33 m<sup>2</sup>/g (Fig. 3.1a). Compared with Eu<sub>2</sub>O<sub>3</sub>-A, homogeneous oval Eu<sub>2</sub>O<sub>3</sub>-B has bigger particle size (~ 130 nm) (Fig. 3.1b) and smaller SSA (8.47 m<sup>2</sup>/g). Because these Eu<sub>2</sub>O<sub>3</sub>-A and Eu<sub>2</sub>O<sub>3</sub>-B powders consist of fine particles and possess large SSA, chemical reactivity of this Eu<sub>2</sub>O<sub>3</sub> powder is expected to be extremely high. Eu<sub>2</sub>O<sub>3</sub>-C powders are prepared from Eu(NO<sub>3</sub>)·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> by the coprecipitation method. The precipitate was calcined at 800 °C for 1 hr. The particle size of Eu<sub>2</sub>O<sub>3</sub>-C with needle-like shape is ~ 2.5 µm\*50 nm (top right of Fig. 3.1c). The Eu<sub>2</sub>O<sub>3</sub>-C plate is easier to break due to the existence of some stoma (center of Fig. 3.1c).





Figure 3.1 TEM images of the  $Eu_2O_3$  powder

Figure 3.2 shows representative XRD patterns of synthetics with sulfurization at 500 ~1050 °C for 0.5 ~ 8 hr and GFR of 1.67 mL/s. In Fig. 3.2a, single phase  $Eu_3S_4$  formed by the sulfurization of  $Eu_2O_3$ -A at 500°C for 8 hr. Single  $Eu_3S_4$  can be gained

from Eu<sub>2</sub>O<sub>3</sub>-A only at 500 °C for longer than 0.5 hr. The intensities of EuS characteristic peaks strengthened while those of Eu<sub>3</sub>S<sub>4</sub> weakened following with sulfurization temperature increasing from 600 °C to 800 °C. Single phase EuS can be obtained at 800 °C for 3 hr or above 900 °C for 0.5 hr.

For the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-B, it is impossible to prepared single phase Eu<sub>3</sub>S<sub>4</sub> at 500 °C for 0.5 - 8 hr. Different with the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A, weak characteristic peaks of residual Eu<sub>2</sub>O<sub>3</sub> always existed. The transformation of Eu<sub>3</sub>S<sub>4</sub>-to-EuS started from 600 °C, which is similar with that of Eu<sub>2</sub>O<sub>3</sub>-A. However, the transformation process cannot complete due to the residual Eu<sub>2</sub>O<sub>2</sub>S. Single phase EuS cannot be sulfurized at 800 °C even for 8 hr with different CS<sub>2</sub>-gas flow rate (0.83 mL/s - 1.67 mL/s). EuS can be prepared at 900 °C for 2 hr or above 1000 °C for 0.5 hr.





Figure 3.2 XRD patterns of synthetics with sulfurization at 500 ~1050 °C for 0.5 ~ 8 hr and GFR of 1.67 mL/s

Figure 3.3 shows typical XRD patterns of the products prepared by  $CS_2$  sulfurization of  $Eu_2O_3$ -A powder at 673-1073 K for 0.5-8 hr. The sulfurization reaction started at 673 K and diffraction peaks of  $Eu_3S_4$  and  $EuS_2$  were detected (Fig. 2a).  $Eu_3S_4$ , as a single product, was obtained via sulfurization at 773 K for 4 hr (Fig. 2b, JCPDS standard card PDF 01-074-7272). Ananth et al. [95] attempted to synthesize  $Eu_3S_4$  from a 3:4 mixture of Eu and S powder using a direct reaction method in a sealed tube. That reaction yielded an unknown product at 773 K [95]. In the present study, all the peaks were identified. When the sulfurization temperature was increased to 873 K, weak diffraction peaks of EuS and  $Eu_2O_2S$  were observed, but the main phase was  $Eu_3S_4$  (Fig. 2c). Single-phase EuS was obtained via sulfurization at temperatures above 1073 K for 8 hr (Fig. 2d, JCPDS standard card PDF03-065-5080). Reduction of europium to the divalent state would increase the number of 4f electrons to seven, which is a half-filled level and thus a stable state.



Figure 3.3 XRD patterns of the products prepared by CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A powder at 673-1073 K for 0.5-8 hr.

Figure 3.4 shows the dependence of the lattice parameters of  $Eu_3S_4$  (on the break) and EuS (below the break) on the sulfurization conditions. It is reported that the lattice parameters of cubic  $Eu_3S_4$  and EuS are 8.534 Å (PDF card 01-074-7272) and 5.97 Å [109], respectively. In the sulfurization temperature range where  $Eu_3S_4$  was detected, as shown in Figure 3.4, the lattice constant of  $Eu_3S_4$  tended to decrease as the sulfurization temperature and time decreased. In the low sulfurization temperature range where  $Eu_3S_4$  presented, the lattice constant of EuS did not depend on the sulfurization time and remained constant at 5.97 Å. In the high sulfurization temperature range, the lattice constant of EuS gradually decreased as the sulfurization

temperature increased in the case of a short sulfurization time. In the high sulfurization temperature range where single-phase EuS was obtained, the lattice constant was smaller in the case of a long sulfurization time than in the case of a short sulfurization time.



Figure 3.4 Lattice parameters of Eu<sub>3</sub>S<sub>4</sub> and EuS

Table 3.2 shows chemical composition of synthetic EuS from sulfurization of  $Eu_2O_3$ . For a low sulfurization temperature, impurity oxygen remained in the  $Eu_3S_4$  powder. The content of impurity oxygen declined from 0.89% in the  $Eu_3S_4$  powder (sulfurized at 500 °C for 8 hr) to 0.11% in the EuS powder (sulfurized at 1000 °C for 8 hr). On the other hand, the amount of impurity carbon increased from 0.05% (sulfurized at 800 °C for 8 hr) to 0.26% (sulfurized at 1000 °C for 8 hr) in the EuS powder due to the decomposition of CS<sub>2</sub> gas. Based on the mole ratio of Eu to S in the EuS powder, S deficiency was observed for the short sulfurization temperature, S was enriched, i.e., Eu was deficient. It is deduced that EuS possesses a solid solution range and the Eu deficiency was more clearly observed.

Table 3.2 Chemical composition of synthetics by sulfurized Eu<sub>2</sub>O<sub>3</sub>-A

Product	Temp.	Time	Mass(O)	Mass (C)	Mass(Eu)	Mass (S)	Mole Eu/S
Eu <sub>3</sub> S <sub>4</sub>	500 °C	8 hr	0.89%	0.12%	77.9%	21.0%	0.7825
EuS	800 °C	3 hr			81.18%	17.09%	0.9980

EuS	800 °C	8 hr	0.52%	0.05%	82.5%	17.7%	1.0171
EuS	900 °C	0.5 hr			82.02%	17.27%	0.9982
EuS	1000 °C	0.5 hr			82.25%	17.32%	0.9983
EuS	1000 °C	8 hr	0.11%	0.26%	82.4%	18%	1.0356

3.3.2 Influence of sulfurization conditions on the formation of EuS

The temperature dependences of diffraction intensity of EuS (200), Eu<sub>2</sub>O<sub>2</sub>S (100), Eu<sub>3</sub>S<sub>4</sub> (211), EuS<sub>2</sub> (220) and Eu<sub>2</sub>O<sub>3</sub> (222) formed via CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A at 500 °C - 1050 °C for 0.5, 1, and 8 hr with gas flow rate of 1.67 mL/s are shown in Fig. 3.5a. At a sulfurization temperature of 400 °C, EuS<sub>2</sub> was formed as an intermediate product. Shafer [106] reported that EuS<sub>2</sub> was not formed during H<sub>2</sub>S-gas sulfurization of Eu<sub>2</sub>O<sub>3</sub>. The maximum diffraction intensity of EuS<sub>2</sub> was detected at 400 °C and disappeared at 500 °C. Diffraction intensity of Eu<sub>3</sub>S<sub>4</sub> increased gradually from 400 °C to 500 °C and decreased from 600 °C and finally disappeared at 800 °C. Single phase Eu<sub>3</sub>S<sub>4</sub> was obtained at 500 - 550 °C, which is lower than the temperature at which this single phase was obtained during H<sub>2</sub>S sulfurization, i.e., above 650 °C [106]. Hexagonal Eu<sub>2</sub>O<sub>2</sub>S appeared at 600 - 800 °C for short reaction time of 0.5 hr or 1 hr. For longer sulfurization time of 8 hr, Eu<sub>2</sub>O<sub>2</sub>S disappeared at 600 °C. Single EuS phase was finally formed at 800 °C for 8 hr.

With an increase in the sulfurization temperature,  $Eu_2O_2S$  was detected with low intensity in the temperature range of phase transformation from  $Eu_3S_4$  to EuS, where  $Eu_3S_4$  and EuS coexistent. The temperature range of this phase transformation became narrow as the sulfurization time increased. For a longer sulfurization time of 8 hr, low intensity  $Eu_2O_2S$  peaks were observed at only 600 °C.

Figure 3.5b shows temperature dependences of diffraction intensity of EuS (200), Eu<sub>2</sub>O<sub>2</sub>S (100), Eu<sub>3</sub>S<sub>4</sub> (211), EuS<sub>2</sub> (220) and Eu<sub>2</sub>O<sub>3</sub> (222) formed via the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-B at 500 °C - 1050 °C for 0.5 hr and 8 hr with GFR of 1.67 mL/s. Different with the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A, peaks of Eu<sub>2</sub>O<sub>3</sub>-B did not fade until to 700 °C for 0.5 hr and 600 °C for 8 hr, respectively. Eu<sub>3</sub>S<sub>4</sub> appeared at 500 - 700 °C for short sulfurization of 0.5 hr. However, the decomposition of Eu<sub>3</sub>S<sub>4</sub> finished at 600 °C for 8 hr. Single phase EuS can be synthesized by the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-B at 1000 -

1050 °C for 0.5 hr or 900 °C for 8 hr.





Figure 3.5 Temperature dependences of diffraction intensity of EuS (200), Eu<sub>2</sub>O<sub>2</sub>S (100), Eu<sub>3</sub>S<sub>4</sub> (211), EuS<sub>2</sub> (220) and Eu<sub>2</sub>O<sub>3</sub> (222) formed via CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A at 500 °C - 1050 °C for 0.5, 1, and 8 hr with gas flow rate of 1.67 mL/s
3.3.3 Morphology and specific surface area of EuS particles

Figure 3.6 shows typical SEM micrographs of synthetics formed by the sulfurization of  $Eu_2O_3$ -A powders. The shape of  $Eu_3S_4$  produced at 500 °C for 0.5 hr with GFR of 1.67 mL/s (Fig. 3.6a) is similar with that of  $Eu_2O_3$ -A (Fig. 3.1a). Following sulfurization temperature increased to 800 °C,  $Eu_3S_4$  phase transformed to EuS phase (Fig. 3.6b). The transformation of  $Eu_3S_4$ -to-EuS was accelerated by increase of impurity content, just like the effecting of carbon on the sintered  $La_2S_3$  powders [112]. The important point to note is the shape of single EuS is similar with that of  $Eu_2O_3$ -A.



(b) Eu<sub>2</sub>O<sub>3</sub>-A sulfurized at 600°C





Figure 3.6 SEM micrographs of  $Eu_3S_4$  and EuS formed by the sulfurization of  $Eu_2O_3$ -A

Figure 3.7 shows SEM micrographs of the sulfurization products formed by sulfurization at 600-800 °C for 3 hr. Single phase EuS was obtained at 800 °C for the same sulfurization time. Similar to  $Eu_3S_4$ , agglomeration of primary EuS particles generated secondary particles. As shown in the SEM images, the average size of the primary particles tended to become larger as the sulfurization temperature increased.





Figure 3.7 SEM micrographs of the sulfurization products formed by sulfurization at 600-800 °C for 3 hr

Figure 3.8 shows SEM micrographs of EuS formed by the sulfurization of  $Eu_2O_3$ -B at 900 - 1050 °C for 0.5-2 hr with GFR of 1.67 mL/s. Fig. 3.8a shows the partial agglutination of single EuS phase. In Fig. 3.8b, the sulfurization product has larger particle size than that of EuS in Fig. 3.8a, inferring that EuS particle grows as the temperature increases to 1050 °C. Gas flow rate has little effect on the morphology of sulfurization products as shown in Fig. 3.8d - f. The differences of  $Eu_2O_3$ -A and  $Eu_2O_3$ -B are smaller as shown in Fig. 3.1, but the shapes of synthetic EuS are differences.



Figure 3.8 SEM micrographs of EuS formed by the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-B at 900 - 1050 °C for 0.5-2 hr with GFR of 1.67 mL/s

Figure 3.9 shows SEM micrographs of EuS produced by the sulfurization of  $Eu_2O_3$ -C powders with GFR of 1.67 mL/s. In Fig. 3.9a and Fig. 3.9b, grain size and shape of EuS are different with that of primary  $Eu_2O_3$ -C particles (Fig. 3.1c), which is same with H<sub>2</sub>S-gas sulfurization of  $Eu_2O_3$  nanowires [109]. Both variation of the oxidation state of europium from trivalent to divalent and the anion exchange process for  $Eu_2O_3$  to EuS need high sulfurization temperature, which destroys the morphology of the oxide nanowires resulting in highly sintered agglomerated materials [109]. Moreover, grain size of synthetic EuS became larger with the rising of temperature.



Figure 3.9 shows SEM micrographs of EuS produced by the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-C powders with GFR of 1.67 mL/s

Figure 3.10 shows particle size distributions of  $Eu_2O_3$ ,  $Eu_3S_4$  sulfurized at 500 °C and EuS powders sulfurized at 800 °C, respectively. The average particle size of  $Eu_2O_3$  is 4.15 µm. Compared with  $Eu_2O_3$  powder, the distribution of synthetic  $Eu_3S_4$  and EuS reflects a broad range of particle sizes with poor uniformity. The average particle size of synthetic  $Eu_3S_4$  is 6.95 µm, which is smaller than that of EuS (11.37 µm). Both  $Eu_3S_4$  and EuS have larger particles than that of  $Eu_2O_3$ .



Figure 3.10 Particle size distributions of Eu<sub>2</sub>O<sub>3</sub>, Eu<sub>3</sub>S<sub>4</sub>, and EuS The SSA of the sulfurization products obtained from Eu<sub>2</sub>O<sub>3</sub>-A at 400 - 800 °C for 1-3 hr are summarized in Fig. 3.11. The SSA of all sulfurization products was smaller than that of the parent Eu<sub>2</sub>O<sub>3</sub>-A (9.37 m<sup>2</sup>/g), indicating that the SSA of the synthetics decreased and the particle size increased during the sulfurization process. It was confirmed that the SSA decreased as the sulfurization temperature and time increased. This is due to grain growth with increasing sulfurization temperature and time, which leads to the reduction of the SSA. When EuS was formed subsequently to the formation of single-phase Eu<sub>3</sub>S<sub>4</sub> at 500 °C, the SSA declined to a lesser extent, and eventually the SSA increased slightly. The density of EuS (5.71 g/cm<sup>3</sup>) is less than that of Eu<sub>3</sub>S<sub>4</sub> (6.26 g/cm<sup>3</sup>); thus, the decrease in the density caused a slight increase in the volume of the sample when the transformation described in Equation (1) occurred to

$$Eu_3S_4(s) \to 3 EuS(s) + 1/2 S_2(g)$$
 (1)

form EuS. This also led to an increase of the SSA.


Figure 3.11 SSA of the sulfurization products obtained from Eu<sub>2</sub>O<sub>3</sub>-A at 400 - 800 °C for 1-3 hr 3.3.4 Thermodynamic analysis of sulfurization process

CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub> is a complex reaction process. The proposed reactions that occur during CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub>, in addition to that in Equation (1), are described below. The sulfurization reaction of H<sub>2</sub>S gas is also described below. Eu<sub>2</sub>O<sub>3</sub> (s) + 3CS<sub>2</sub> (g)  $\rightarrow$  2/3Eu<sub>3</sub>S<sub>4</sub> (s) + 3COS (g) + 1/6S<sub>2</sub> (g) [113] (2) Eu<sub>2</sub>O<sub>3</sub> (s) + CS<sub>2</sub> (g)  $\rightarrow$  Eu<sub>2</sub>O<sub>2</sub>S (s) + COS (g) [114] (3) Eu<sub>2</sub>O<sub>3</sub> (s) + 3/2CS<sub>2</sub> (g)  $\rightarrow$  2EuS (s) +1/2S<sub>2</sub> (g) + 3/2CO<sub>2</sub> (g) (4)

$$Eu_2O_3(s) + 3/2CS_2(g) \to 1/2 EuS_2(s) + 1/2Eu_3S_4(s) + 3/2CO_2(g)$$
(5)

$$EuS_{2}(s) \rightarrow 1/3Eu_{3}S_{4}(s) + 1/3S_{2}(g)$$

$$Eu_{2}O_{3}(s) + EuS_{2}(s) \rightarrow 3/2Eu_{2}O_{2}S(s) + 1/4S_{2}(g)$$
(6)
(7)

$$Eu_2O_3(s) + 3H_2S(g) \rightarrow 2EuS(s) + 1/2S_2(g) + 3H_2O(g)$$
 (8)

$$Eu_2O_3(s) + EuS(s) + 1/4S_2(g) \rightarrow 3/2Eu_2O_2S(s)$$
 (9)

 $Eu_2O_3(s) + 1/2Eu_3S_4(s) \to 3/2Eu_2O_2S(s) + 1/2EuS(s)$ (10)

The temperature dependences of the standard free-energy changes ( $\Delta G^{\circ}$ ) for most of these reactions were calculated from the thermodynamic data [113-115] as shown in Fig. 3.12. The sulfurization reaction is considered to proceed mainly due to Equations (2), (3), and (4). Comparison of Equation (2) with Equation (3) shows that the negative value of  $\Delta G^{\circ}$  is larger in Equation (2) than that of Equation (3) at low temperatures and smaller at high temperatures. Therefore, Eu<sub>3</sub>S<sub>4</sub> and Eu<sub>2</sub>O<sub>2</sub>S are predicted to be formed at low and high temperatures, respectively. Since  $\Delta G^{\circ}$  in Equation (4) exhibits positive and negative values at low and high temperatures, respectively, EuS is predicted to be formed only at high temperatures. Shafer et al. [106] reported that when the sulfurization of Eu<sub>2</sub>O<sub>3</sub> powder was performed using H<sub>2</sub>S gas until equilibrium was reached, Eu<sub>2</sub>O<sub>2</sub>S was formed at 400 - 550 °C, Eu<sub>2</sub>O<sub>2</sub>S and Eu<sub>3</sub>S<sub>4</sub> were formed at 575 -650 °C, Eu<sub>3</sub>S<sub>4</sub> containing a small amount of EuS was formed at 700 °C, and single-phase EuS was obtained at 950 °C or higher. Therefore, this reaction mechanism can be generally predicted from Fig. 3.12.



Figure 3.12 Temperature dependence of standard free-energy change for the reactions In the present research, when Eu<sub>3</sub>S<sub>4</sub> was first formed from Eu<sub>2</sub>O<sub>3</sub>, EuS<sub>2</sub> was formed instead of Eu<sub>2</sub>O<sub>2</sub>S, and a small amount of Eu<sub>2</sub>O<sub>2</sub>S was formed in the temperature range where Eu<sub>3</sub>S<sub>4</sub> and EuS coexisted. Although the particle size of Eu<sub>2</sub>O<sub>3</sub> used by Shafer et al. [106] is unknown, the particle size of Eu<sub>2</sub>O<sub>3</sub> is smaller. Therefore, the excellent reactivity of Eu<sub>2</sub>O<sub>3</sub>, the formation of EuS<sub>2</sub> instead of Eu<sub>2</sub>O<sub>2</sub>S, and the formation of Eu<sub>2</sub>O<sub>2</sub>S, in which trivalent Eu (as a component of Eu<sub>3</sub>S<sub>4</sub>) utilized the oxygen in Eu<sub>3</sub>S<sub>4</sub>, can be explained. When Equation (4) is compared with Equation (8),

it can be understood that the reactivity of  $CS_2$  gas is superior to that of  $H_2S$  gas. The reaction mechanism that is operative in the present study is thought to differ from that performed by Shafer et al. because of the excellent reactivity of  $CS_2$  gas and  $Eu_2O_3$  utilized in the present study.

Figure 3.13 summarizes the relationship between the sulfurization conditions and the products from the sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A. No reaction was observed at 300 °C. A mixture of Eu<sub>2</sub>O<sub>3</sub>, EuS<sub>2</sub>, and Eu<sub>3</sub>S<sub>4</sub> was synthesized at 400 °C with a treatment time of less than 3 hr. When the sulfurization time increased from 3 to 8 hr, EuS<sub>2</sub> and Eu<sub>3</sub>S<sub>4</sub> became the prominent phases. For sulfurization at 500 °C, single-phase Eu<sub>3</sub>S<sub>4</sub>was formed regardless of the sulfurization time. At 600 °C, EuS was also formed in addition to Eu<sub>3</sub>S<sub>4</sub>, and a small amount of Eu<sub>2</sub>O<sub>2</sub>S was also detected. Subsequently, single-phase EuS was obtained by sulfurization at 800 °C for 3 hr, and at 900 °C for 0.5 hr; i.e., the sulfurization time decreased as the sulfurization temperature increased. The results show that the reaction sequence with increasing temperature was as follows: Eu<sub>2</sub>O<sub>3</sub>  $\rightarrow$  EuS<sub>2</sub> (400 °C)  $\rightarrow$  Eu<sub>3</sub>S<sub>4</sub> (400 - 500 °C)  $\rightarrow$  EuS (Eu<sub>2</sub>O<sub>2</sub>S above 600 °C). Europium was reduced from the trivalent state to the divalent state with increasing sulfurization temperature.



Figure 3.13 Relationship of sulfurization products with sulfurization conditions for  $Eu_2O_3$ -A

# 3.4 Heat treatment of synthesized Eu<sub>3</sub>S<sub>4</sub>

In Chapter 2.3, the phase transformation from orthorhombic  $Yb_2S_3$  to hexagonal  $Yb_2S_3$  reportedly occurred when heat treatment was performed at 1000 °C for 3 hr in an Ar/CS<sub>2</sub> atmosphere, but this phase transformation did not occur under the same conditions in an Ar atmosphere [116]. Moreover, hexagonal  $Yb_2S_3$  was transformed to  $Yb_3S_4$  with treatment at 1000 - 1050 °C for 12 hr under Ar atmosphere. To confirm the stability of Eu<sub>3</sub>S<sub>4</sub> under different atmospheres, synthesized Eu<sub>3</sub>S<sub>4</sub> was heat treated for 1 hr under Ar/CS<sub>2</sub> or Ar atmosphere. The XRD patterns of the heat-treated products derived from Eu<sub>3</sub>S<sub>4</sub> are shown in Figure 3.14. Eu<sub>3</sub>S<sub>4</sub> sulfurized at 500 °C for 8 hr was employed as the starting material for heat treatment.

XRD patterns of the heat-treated products derived from  $Eu_3S_4$  are shown in Figure 3.14. The synthesized  $Eu_3S_4$  powders underwent phase transition at 600 °C under Ar/CS<sub>2</sub> atmosphere. Transformation of  $Eu_3S_4$  to EuS was completed at 700 °C.

However, weak characteristic peaks of  $Eu_2O_2S$  remained after heat treatment at 800 °C under Ar atmosphere. The striking differences between these two atmospheres are the reducibility and sulfur vapor pressure. The difference between Ar/CS<sub>2</sub> or Ar atmosphere is that the reductive gas CS<sub>2</sub> can avoid the formation of  $Eu_2O_2S$  compared with Ar atmosphere. The generated EuS is very easy to be oxidation under Ar atmosphere. On the other hand, the sulfur vapor pressure under Ar/CS<sub>2</sub> atmosphere is higher than that of Ar atmosphere. Theoretically, the decomposition of  $Eu_3S_4$  is inhibited so the reaction rate may be slow under Ar/CS<sub>2</sub> atmosphere.



Figure 3.14 XRD patterns of synthetics from Eu<sub>3</sub>S<sub>4</sub> under Ar or Ar/CS<sub>2</sub> atmosphere To clearly illustrate the influence of sulfur vapor pressure, representative XRD
patterns of the reaction products from Eu<sub>3</sub>S<sub>4</sub> treated under vacuum are shown in Fig.
3.15. During the annealing process, Eu<sub>3</sub>S<sub>4</sub> was stable at 500 °C and the vapor pressure of sulfur increased due to the decomposition of Eu<sub>3</sub>S<sub>4</sub>. Diffraction peaks of EuS were

observed with treatment at 550 °C for 1 hr, and single-phase EuS was formed by annealing at 600 °C. Furthermore, when EuS was annealed at the higher temperature of 1500 °C, no decomposition occurred due to the high melting point of EuS. The phase transformation of Eu<sub>3</sub>S<sub>4</sub>-to-EuS is similar with that of Yb<sub>3</sub>S<sub>4</sub>-to-YbS at 1500 -1550 °C under vacuum. The crystal structures of Eu<sub>3</sub>S<sub>4</sub> and EuS are Th<sub>3</sub>P<sub>4</sub>-type (space group I-43d) and NaCl-type crystal structure (space group Fm3m), respectively. Moreover, Eu<sub>3</sub>S<sub>4</sub> included bivalent and trivalent Eu ion, but EuS usually contained bivalent Eu ion. Bivalent Eu ion is more stable than trivalent Eu at high temperature, so Eu<sub>3</sub>S<sub>4</sub> transformed to EuS at high temperature.



Figure 3.16 shows lattice parameters of EuS/Eu<sub>3</sub>S<sub>4</sub> tinder vacuum Figure 3.16 shows lattice parameters of EuS/Eu<sub>3</sub>S<sub>4</sub> from Eu<sub>3</sub>S<sub>4</sub> treated at 400-1050 °C for 1 hr under Ar or Ar/CS<sub>2</sub> atmospheres. Compared with initial Eu<sub>3</sub>S<sub>4</sub>, lattice parameter of Eu<sub>3</sub>S<sub>4</sub> is about 8.53 Å and has no obvious change after treated at 400 °C or 600 °C under Ar atmosphere. Lattice parameter of EuS is almost same with that of sulfurized EuS (5.97 Å). It suggested that both methods, CS<sub>2</sub> sulfurization and heat treatment, can be employed to fabricate high pure EuS.



Figure 3.16 Lattice parameters of EuS/Eu<sub>3</sub>S<sub>4</sub> from treated Eu<sub>3</sub>S<sub>4</sub> Figure 3.17 shows SEM micrographs of the products derived from heat-treatment of synthesized Eu<sub>3</sub>S<sub>4</sub> under Ar/CS<sub>2</sub> atmosphere. The particle size is similar to that obtained via direct CS<sub>2</sub> sulfurization of Eu<sub>2</sub>O<sub>3</sub> at 600 - 800 °C as shown Fig. 3.7. In the case of Eu<sub>3</sub>S<sub>4</sub> as well as Eu<sub>2</sub>O<sub>3</sub>, fine primary particles agglomerated to form secondary particles, and the average size of the secondary particles tended to increase as the heat treatment temperature increased. The average size of the primary particles was constant up to the heat treatment temperature of 800 °C, regardless of the types of products.









Figure 3.17 SEM micrographs of the products derived from heat-treatment of synthesized  $Eu_3S_4$  under  $Ar/CS_2$  atmosphere

Table 3.3 shows chemical compositions of synthetics by treated Eu<sub>3</sub>S<sub>4</sub> powders at 500 - 800 °C for 1 hr under Ar/CS<sub>2</sub> or Ar gas. There is a phase transformation of synthetic Eu<sub>3</sub>S<sub>4</sub> powders with Th<sub>3</sub>P<sub>4</sub> structure to EuS powders with NaCl structure. The impurity content lessened during this phase transformation following with temperature increase. Moreover, impurity content of EuS treated under Ar/CS<sub>2</sub> gas is lower than that of EuS treated under Ar gas. This result suggested that impurity oxygen can be removed by heat treatment under Ar/CS<sub>2</sub> atmosphere. The phase transformation from Eu<sub>3</sub>S<sub>4</sub> to EuS differs from the phase transformation of light rare-earth sesquisulfides R<sub>2</sub>S<sub>3</sub> (R = La, Ce, Sm, Nd, and Gd), in which the composition does not change.

	Heat-treatment			Composition (mass %)		
Synthetics	K	hr	Gas	Eu	S	Impurity
Eu <sub>3</sub> S <sub>4</sub>	773	1	Ar/CS <sub>2</sub>	78.44	15.49	6.06
Eu <sub>3</sub> S <sub>4</sub> / EuS	873	1	Ar/CS <sub>2</sub>	79.08	16.65	4.27
EuS	973	1	Ar/CS <sub>2</sub>	82.45	17.36	0.19
EuS	1073	1	Ar/CS <sub>2</sub>	82.54	17.37	0.09
EuS	1073	1	Ar	82.02	17.27	0.71

Table 3.3 Chemical compositions of synthetics by heat-treated Eu<sub>3</sub>S<sub>4</sub> at 500 - 800  $^{\circ}$ C

The results of heat-treatment study revealed that enrichment of sulfur was effective for the sulfurization of impurity phase  $Eu_2O_2S$ . The decomposition reaction of  $Eu_3S_4$  was confirmed to proceed easily under reduced pressure.

#### 3.5 Sintering and large magnetocaloric effect of synthesized EuS

3.5.1 Sintering of synthetic EuS powder

Representative XRD patterns of synthetics from sulfurized EuS powders at  $1000^{\circ}$ C ~  $1400^{\circ}$ C for 3 hr are shown in Figure 3.18. Single phase EuS compacts can be obtained for all the sintering temperature ranges. There is no characteristic peak of Eu<sub>2</sub>O<sub>2</sub>S.



Fig. 3.18 XRD patterns of sintered EuS compacts at 1000 -1400 °C for 3 hr

Figure 3.19 showed SEM image of the sintered EuS for the cross section of fracture surface at 1000 -1400 °C for 3 hr. The EuS powders were from the sulfurization of  $Eu_2O_3$ -B by  $CS_2$  gas. The sintered EuS is entirely homogeneous and there is no obviously preferred orientation. In addition, the particle size of the EuS grain becomes larger as sintering temperature increases. On the other hand, the brittle fracture is within the grain boundary and the existence of cleavage plane can explain the crack of sintered EuS.



Fig. 3.19 SEM micrograph of EuS sintered at 1000°C (a), 1200 °C (b), and 1400 °C (c) for 3 hr

## 3.5.2 Magnetization of polycrystalline EuS compacts

Figure 3.20 showed Magnetization M(T) and inverse susceptibility of polycrystalline EuS compact as functions of temperature in a field of 100 Oe. The magnetization of polycrystalline EuS is smaller than that of single crystal EuS, about The PM to FM transition for polycrystalline EuS occurred at around the defined Curie temperature  $T_c = 16.8$  K. the M(T) behavior conform the Curie-Weiss rule with the values of PM Curie temperature  $\theta_P=16.95$ . This Curie temperature is similar with that of single crystal EuS. However, the field cooling (FC) and zero-field-cooling (ZFC) curves have some difference over the measure temperature range. This result indicates that there are some thermomagnetic irreversibility and magnetic anisotropy for polycrystalline EuS compact.



Figure 3.20 Temperature dependences of FC magnetization of polycrystalline EuS

In order to investigate the influence of applied magnetic field on the magnetocaloric property of polycrystalline EuS, the isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T at around the magnetic transition temperature (16.5 K). Figure 3.21 shows the field dependence of magnetization for sintered EuS at the temperature range of 10 - 30 K. EuS bulks were sintered by spark plasmas sintering under vacuum of  $7 *10^{-3}$  Pa at 1000 °C for 3 hr from EuS powders, which were prepared by sulfurization of Eu<sub>2</sub>O<sub>3</sub>-B powders at 900 °C for 2 hr. The density of sintered EuS compact is 4.9 g/cm<sup>3</sup> and the grain size of sintered EuS bulk is about 5 µm. XRD pattern suggested sintered EuS bulk was single phase without characteristic peak of Eu<sub>2</sub>O<sub>2</sub>S. From Fig. 3.21, the M-H characteristics

were differences in different temperature ranges. The sintered EuS showed a paramagnetic-to-ferromagnetic transition at below 1 T and then tends to saturate with the rising of magnetic field. A similar behavior has been observed in single crystal EuS applied along the [100] and [110] direction [103].



Fig. 3.21 Magnetization of polycrystalline EuS as a function of field The relationship between magnetization M(H, T)/ M(H, B) for polycrystalline EuS and temperature or magnetic field are shown in Fig. 3.22. EuS compact was sintered by spark plasmas sintering under vacuum of  $7 * 10^{-3}$  Pa at 1600 °C from EuS powders, which were prepared by sulfurization of Eu<sub>2</sub>O<sub>3</sub>-A powders. As seen in Figure 3.21a, M(H, T) showed the ferromagnetic behavior and had different values for a certain field at low temperatures, which is different with that of single crystal EuS with almost the same value for a given and temperature. The magnetization reached the saturation before 1 T at low temperature. This trend became weak following the rising of temperature and the magnetization increases nearly linearly with an increase in magnetic field and this slope reduced with the rising of temperature from 34 K to 50 K. Magnetization lessened with the increase of temperature for a certain field. A slight nonlinearity in the M - H curves is noticed at low temperatures for fields much higher than 4T, which may be ascribed to the existence of impurity of residual carbon or oxygen atom caused by the sulfurization process.

Figure 3.21b showed the temperature dependence of the magnetization of polycrystalline EuS at various magnetic fields. For polycrystalline EuS, a clear jump for magnetization was observed at  $T_C$  for the magnetic fields less than 0.6 T. EuS



exhibits smooth temperature variation of the magnetization particularly at high fields.

Figure 3.21 Magnetization of polycrystalline EuS as a function of field (a) and temperature (b)

The Arrott plots of polycrystalline EuS compound (from Eu<sub>2</sub>O<sub>3</sub>-B) sintered at 1000 °C for 3 hr are shown in Fig. 3.22. The negative slope of the Arrott plot confirmed the occurrence of a second order PM-to-FM phase transition. The isothermal magnetic entropy changes have been calculated from the isothermal magnetization data by employing Maxwell's relationship  $\Delta S(T, H) = \int_0^H (\frac{\partial M}{\partial T})_H dH$ . The entropy changes  $\Delta S$  for different magnetic field changes as a function of temperature are given in Fig. 3.23. The  $\Delta S$  of polycrystalline show peaks around T<sub>c</sub> and the maximum values of  $\Delta S$  are obtained to be 16.76 J/Kg/K and 28.4 J/Kg/K for the field changes of 2 T and 5 T, respectively. Though these values are slight smaller than those of single crystal EuS under the same magnetic field change, the preparation

process is simple and the raw material  $Eu_2O_3$  powders are cheaper and easier to storage. Moreover, the entropy changes  $\Delta S$  were connected with grain size of sintered EuS [117], grain size and  $\Delta S$  will be optimize in further study.



Fig. 3.22 The Arrott plots of polycrystalline EuS sintered at 1000 °C for 3hr from  $Eu_2O_3$ -B



Fig. 3.23 Magnetic entropy change of polycrystalline EuS from Eu<sub>2</sub>O<sub>3</sub>-B Figure 3.24 shows Arrott plots of polycrystalline EuS (from Eu<sub>2</sub>O<sub>3</sub>-A) in which the appearance of the inflection point confirms the occurrence of a magnetic transition from the paramagnetic to ferromagnetic ordering at above T<sub>c</sub>. The negative slop of the Arrott plots (M<sup>2</sup> versus H/M) suggests that it is a second order phase transformation.



Figure 3.24 The Arrott plots ( $M^2$  versus H/M) of polycrystalline EuS from Eu<sub>2</sub>O<sub>3</sub>-A The change in magnetic entropy of polycrystalline EuS (from Eu<sub>2</sub>O<sub>3</sub>-A) is displayed in Figure 3.25 as a function of the temperature for different magnetic fields. The absolute value of  $\Delta S$  first increased and began to decrease after reaching a maximum value. Moreover, the corresponding temperature for maximum  $\Delta S$  increased slightly from 17.47 K for  $\Delta H = 1T$  to 17.97 K for  $\Delta H = 5T$ . A large MCE was observed at above Curie temperature. The peak values of  $\Delta S$  under applied fields of 1, 2, and 5 T are 2.02, 3.57, and 6.32 J/mol/K, respectively. It need to emphasize that the observed  $\Delta S$  value for polycrystalline EuS is similar with that of single crystal EuS prepared with the more complex process. Such a high magnitude of  $\Delta S$  was rarely observed in polycrystalline rare-earth monosulfides or sesquisulfides.



Figure 3.25 Magnetic entropy change of EuS as a function of temperature calculated from the magnetization data 3.5.3 Specific heat of polycrystalline EuS compacts

To calculate the adiabatic temperature change  $\Delta T_{ad}$  and verify the accuracy of the magnetic entropy change estimated based on the Maxwell relation, the temperature dependence of specific heat C(T) of EuS (from Eu<sub>2</sub>O<sub>3</sub>-A) was also measured in magnetic fields of zero and 5 T as illustrated in Fig. 3.26. The C(T) curve shows a large peak at around 16.4 K under the zero field. Following the increase of magnetic field, the peak becomes weak and disappeared. The specific heat peak is almost completely smoothed out at 5 T.



Figure 3.26 Specific heat of EuS measured at different magnetic field Figure 3.27a showed the calculated results of entropy based on the specific heat data (Figure 3.26). The entropy for polycrystalline EuS has a convex at the about Curie temperature under zero magnetic field. Entropy change of EuS can be calculated by using  $\Delta S_m = \Delta S = S(H, T)-S(0, T)$ , where,  $S(H, T) = \int_0^T [C(H, T)/T] dT$  as shown in Fig. 3.27b. It can be observed from this figure that the calculated results from calorimetric method are slightly smaller than these from the magnetization results and the Maxwell relation.



Figure 3.27 Calculated entropy value and change of polycrystalline EuS

To get more believable entropy data and reduce the calculated error, the entropy for polycrystalline EuS (from Eu<sub>2</sub>O<sub>3</sub>-A) was calculated from the combination of the calorimetric and magnetic data as shown in Figure 3.28. The entropy data from C(T) data under the field of 5T was chosen as the basis (marked as S(5T)). The revised entropy of polycrystalline EuS under zero magnetic field (marked as S(0T)) is computed from the direct plus for S(5T) and  $\Delta$ S(5T) from the magnetic data. The revised entropy under the field of 1T and 3T can be obtained from the plus of S(0T) with corresponding entropy change from the magnetic data. The revised entropy by matching the specific heat and the magnetization data had a high degree of reliability.



Figure 3.28 the revised entropy for polycrystalline EuS from specific heat and magnetization data

The relative cooling power (RCP) is an important parameter for a magnetic refrigerant material, which is usually defined as RCP =  $|\Delta S_{max} * \delta T_{FWHM}|$ , where  $\Delta S_{max}$  is the maximum of  $\Delta S$  from Fig. 3.25 and  $\delta T_{FWHM}$  is the full width at half corresponding maximum of  $\Delta S$ . The  $\Delta S_{max}$  and RCP were calculated with the above equation as shown in Fig. 3.29. Both  $\Delta S_{max}$  and RCP have the very large values and increase monotonically with increasing  $\Delta H$ , indicating that polycrystalline EuS has the outstanding magnetic refrigeration property. The RCP values were 69.26 and 125.39 J/mol for  $\Delta H = 3$  T and 5 T, respectively. The RCP for polycrystalline EuS is slightly smaller than that of single crystal (143.94 J/mol)  $\Delta H = 5$  T.



Fig. 3.29 Magnetic field dependences of the maximum magnetic entropy change and the relative cooling power of polycrystalline EuS

3.5.4 Comparison specific heat of polycrystalline and singe crystal EuS

To clearly realize the differences of the magnetocaloric properties between polycrystalline and single crystal EuS, heat capacities for both kinds of EuS under different magnetic fields were compared as shown in Fig. 3.30. The heat capacities values are almost same at lower than 20 K under zero magnetic fields. The heat capacity for paramagnetic polycrystalline EuS phase is slightly smaller than that of single crystal EuS.



Fig. 3.30 Comparison of heat capacity for polycrystalline and single crystal EuS under zero field (a); 1T (b); 3 T (c); and 5 T (d);

## **3.6 Conclusions**

Influences of particle size and specific surface area of  $Eu_2O_3$  powders on the synthesis of EuS were investigated. High sulfurization temperature (750 or 800 °C) and small grain size are necessary for preparation of EuS. Larger specific surface area of  $Eu_2O_3$  is better for fabrication of  $Eu_3S_4$  at low temperature of 500 °C for longer than 0.5 hr. The shape of synthetic EuS is dependent with that of smaller spherical  $Eu_2O_3$  but the morphology of the  $Eu_2O_3$  nanowires was destroyed at high sulfurization temperature. The specific surface area of the sulfurization product lessened as the sulfurization temperature increased, accompanying with phase transformation of

Eu<sub>3</sub>S<sub>4</sub>-to-EuS. According to thermodynamic analysis, CS<sub>2</sub>-gas sulfurization is more effective than that of  $H_2S$ -gas sulfurization due to the formation of unstable EuS<sub>2</sub> phase.

In the evaluation of the effect of heat treatment on the phase transformation from  $Eu_3S_4$  to EuS at a fixed heat treatment time of 1 hr, it was found that heat treatment at 973 K under  $CS_2/Ar$  atmosphere and at 873 K under vacuum yielded single-phase EuS. Heat treatment of  $Eu_3S_4$  powder generated a small amount of  $Eu_2O_2S$  owing to the impurity oxygen in  $Eu_3S_4$  powder. When heat treatment was performed at high temperatures in the  $CS_2/Ar$  atmosphere, the formation of  $Eu_2O_2S$  could be inhibited.

Modifying the characters of  $Eu_2O_3$  is an effective step for the preparation of EuS. Large maximum magnetic entropy change of sintered EuS indicated its excellent refrigeration performance and thus it is possible to be employed as magnetic refrigerant material for liquefaction of hydrogen.

A sintered compact of the ferromagnetic semiconductor EuS that had relative density larger than 95% was synthesized. MCE is studied in the vicinity of its ordering temperature and shown to be close to that of single crystal. S - T diagram of sintered EuS was obtained. These results indicate that sintered EuS has excellent ability as a magnetic refrigerant for hydrogen liquefaction.

# Chapter 4 Synthesis and sintering of samarium rich $SmS_x$ and its electrical property

## 4.1 Introduction

Rare earth sulfides were studied as high temperature thermoelectric materials, for their high thermoelectric performances, high melting point, and self-doping ability [80, 118, 119]. Samarium monosulfide SmS at 17.6 wt% sulfur is a semiconductor material with *n*-type conductivity, crystal lattice of the NaCl type, and a high melting temperature (~2300°C)[120]. Characteristic features of the SmS energy-band structure include the presence of 4f levels of samarium located at Ef = 0.23 eV below the conduction-band bottom and acting as donors[120]. This energy-band structure not only decided the pressure induced discontinuous semiconductor-metal transition due to 4f-5d electron delocalization, but also caused the temperature induced thermal electromotive force and phase transformation by a conduction-electron concentration gradient[72].

Similar with preparation of other binary[121, 122] and ternary sesquisulfide, polycrystalline SmS powders were also prepared by the reaction of H<sub>2</sub>S with samarium bis(trimethylsilyl)amide in tetrahydrofuran (THF) at  $10^{-2}$  torr [123], however, volatile and toxic H<sub>2</sub>S is difficult to handle. Traditionally, single crystal SmS with respective compositions was synthesized from metal samarium and sulfur powder by heating, annealing, cold forming, and atmospheric pressure sintering in a sealed silica ampoule tube. However, this method takes long period and composition control of SmS is estimated to be difficult owing to the large difference of vapor pressure between samarium and sulfur.

Most methods employed metallic Sm powders as Sm source for the fabrication of SmS. Compared with metal Sm powder; samarium hydride (SmH<sub>3</sub>) powders were used to replace Sm powders because SmH<sub>3</sub> powders are easier to storage and cheaper than Sm powders. Moreover, the advantage of SmH<sub>3</sub> is the generation of H<sub>2</sub> which can avoid or resist the oxidation of SmS at a certain degree.

Polycrystalline SmS has a thermoelectric figure of merit ZT ~0.9 with the optimal composition  $SmS_{0.96}^{[124]}$ . If we assume the Carnot efficiency to be 50%, thermoelectric materials with ZT=0.89 enable thermoelectric generation with a maximum theoretical

generating efficiency of 10%. According to the phase diagram of samarium and sulfur [125], solid solution range of single SmS phase is obtained just in the narrow composition part. The thermoelectric properties of SmS depend on the actual composition.

In this study, non-stoichiometric  $SmS_x$  (0.55  $\le x \le 1.2$ ) with different target composition was prepared from the direct reaction between of samarium sesquisulfide ( $Sm_2S_3$ ) and  $SmH_3$  to reaffirm the composition dependency of thermoelectric properties. Furthermore, to avoid contamination from the encapsulated ampoule, a BN crucible was employed as the reaction container under vacuum because of high activity of samarium after the release of hydrogen. The reaction temperature is at 1273K which is slightly lower than conventional research. Further, the synthetic powder was sintered with a pulsed electric current sintering device. Electric transport properties of synthetic  $SmS_x$  ( $0.55 \le x \le 1.07$ ) were investigated in detail.

#### **4.2 Experimental procedure**

### 4.2.1 Synthesis of $SmS_x$ powders

Both Sm<sub>2</sub>S<sub>3</sub> and SmH<sub>3</sub> powders from Kojundo Chemical Laboratory Co., LTD were employed. Compared with synthetic Sm<sub>2</sub>S<sub>3</sub> by CS<sub>2</sub>-gas sulfurization of commercial or synthesized Sm<sub>2</sub>O<sub>3</sub> by co-precipitation, commercial Sm<sub>2</sub>S<sub>3</sub> with large vapor pressure sulfur was employed, which has little impurity carbon. SmH<sub>3</sub> and Sm<sub>2</sub>S<sub>3</sub> were weighed in molar ratio of M (M= 0.5 for SmS<sub>1.2</sub>, 0.8 for SmS<sub>1.07</sub>, 1 for SmS<sub>1.0</sub>, 1.11 for SmS<sub>0.96</sub>, 1.5 for SmS<sub>0.86</sub>, 1.8 for SmS<sub>0.79</sub>, 2 for SmS<sub>0.75</sub>, 2.5 for SmS<sub>0.67</sub>, 3 for SmS<sub>0.60</sub>, and 3.5 for SmS<sub>0.55</sub>). These powders were mixed under vacuum glove box to prevent the oxidation. The mixtures were put on BN crucibles and heated at 1273 K for 3 hr under a vacuum of <  $1.2 \times 10^{-3}$  Pa. Honeycomb Ti foils was placed on the top and one side of BN boat to avoid oxidation. Then the product was milled using a ball mill under vacuum.

The synthetic powders mixed with 10% Si (internal standard substance, purity Company,) were analyzed with X-ray diffraction (XRD, Model Rint-Ultima+, Rigaku Corp., Tokyo, Japan) with monochromatic Cu K $\alpha$  radiation at 40 kV and 20 mA to check phase compositions. Cell parameters of synthetic powders were measured at the scan step of  $1.0 \times 10^{-3}$  degree for 2s.

4.2.2 Sintering of SmS<sub>x</sub> compacts

The synthetic SmS<sub>x</sub> powders (1.2 gram) were mounted in a graphite die of 10.5 mm diameter and consolidated by a pulse electric current sintering (SPS-511S, Sumitomo Coal Mining Co.). The chamber of apparatus was pumped down to 7.0 \*  $10^{-3}$  Pa. The sintering was performed at 1373K-1673K for 1 hr under the applied pressure of 50 MPa. Microstructures of SmS<sub>x</sub> compacts were examined with a scanning electron microscopy (SEM, JSM-5310LV, JEOL Ltd. Tokyo, Japan) to reveal the microstructure and compactness. The chemical compositions of the synthetic SmS<sub>x</sub> were determined by ICP emission spectrometry method (Thermo Fisher SCIENTIFIC iCAP6300DUO) for Sm content and infrared absorption technique (LECO CS844) for sulfur content.

## 4.2.3 Electrical properties of SmS<sub>x</sub> compacts

The thermoelectric transport properties such as Seebeck coefficient and electrical resistivity of the sintered compacts were simultaneously measured under a He atmosphere in the temperature range of 300 - 623 K with a temperature differential method and a four-probe method, respectively (ZEM-2). The typical bars used for these measurements had dimensions of 3mm\*3mm\*5 mm. The power factor was calculated from the earlier of the electrical resistivity and Seebeck coefficient. And based on the former research result of thermal conductivity of SmS, the ZT values were calculated and compared with former results prepared by different method.

#### **4.3 Experimental results**

#### 4.3.1 Synthesis of SmS<sub>x</sub> powders

Figure 4.1 shows XRD patterns of synthetics from the mixture of  $Sm_2S_3$  and  $SmH_3$  reacted at 1000°C for 3h. There are two main reactions to produce  $Sm_3S_4$  and SmS. When the ratio of  $Sm_2S_3$  to  $SmH_3$  is 0.5 or 0.8, there are not enough Sm atoms to reduce  $Sm^{3+}$  of  $Sm_2S_3$  to  $Sm^{2+}$  of SmS. So mix-valence compound  $Sm_3S_4$  phase (PFD card: 01-071-0433) is the main product. The prerequisite to fabricate pure SmS (PFD card: 03-065-5955) is the ratio of  $Sm_2S_3$  and  $SmH_3$  above 1. Following with the increase of  $SmH_3$  content, the surplus Sm atoms have self-doped in SmS crystal. Moreover, some Sm atoms replace S atoms in the SmS crystal[72]. In addition, the characteristic peak of rich samarium metal was not identified even the content of metal samarium in the target above 60%. However, the peak position of synthetic  $SmS_x$  is smaller than that of reported semiconductor SmS (30°) or metallic SmS (31°) [126]

and has a trend to low angle following the increase of Sm content. The peaks shift to small angle behavior suggested the large and increase of lattice parameter of SmS following the rising of the ratio of  $Sm_2S_3$  and  $SmH_3$ .

The behavior of the lattice parameter of  $SmS_x$  with samarium content was shown in Fig. 4.2. When the ratio of starting material is less than 1, reaction product is the mixture of Sm<sub>3</sub>S<sub>4</sub> (theory lattice parameter of 8.556 Å) and semiconductor SmS (theory lattice parameter of 5.97 Å). The variation of lattice parameter of synthetic is connected with the difference of the diameter of  $Sm^{2+}$  (ionic radii of 1.14 Å) and  $Sm^{3+}$ (ionic radii of 0.96 Å). Lattice parameters of synthetic SmS showed a wavy variation following the increase of Sm content. The lattice parameter of SmS is also dependent on the temperature[127], which can influence the value fluctuation of Sm atoms between bivalent and trivalent. When Sm content increased to 53.8%, the solved Sm atom in the SmS crystal expanded lattice parameter to 5.99 Å, which has the same effect and value with the temperature dependence[127]. This value is larger than theory lattice parameter of semiconductor SmS. When Sm atoms were melting in the lattice of generated SmS, Sm atoms may substitute in the position of S atoms[128]. After the substitution, atomic radius of Sm atom is much larger than that of S atom. On the other hand, mutual repulsion between Sm atoms and adjacent Sm atoms becomes large. Both cases may cause lattice expansion.







Fig. 4.2 Lattice parameters of synthetic SmS<sub>x</sub>

Table 4.1 lists the nominal and actual compositions of synthetic  $SmS_x$ . As can be seen from the Table 4.1, when the ratio of starting material is 1, the XRD result of synthesized  $SmS_{1.0}$  is single SmS phase, but it presents some trace amounts of sulfur enrichment in the actual composition. The actual synthetic SmS still cannot form Sm enrichment as the ratio of raw materials increased from 1.11 to 1.8. On the other hand, there exists samarium loss during the reaction process. This caused actual composition of  $SmS_x$  became irregular when the ratio of  $Sm_2S_3$  and  $SmH_3$  is above 2. However, this does not affect the preparation of high samarium enrichment  $SmS_x$  and investigation electrical transport properties of  $SmS_x$ . When the ratio of starting material is 2, the actual content of Sm in the synthetic SmS reached 53.9% (another form:  $Sm_{1.16}S$ ). This actual composition has higher Sm content than that reported normal composition for  $Sm_{1.07}S$  [128], which composition is based on the calculation that one sulfur atom was replaced by Sm atom in the SmS unit cell. This result suggested that when the ratio of raw materials is more than 2, more than one sulfur atom is possibly substituted to Sm sites in the unit cell of SmS.

Nominal composition of SmS				Actual composition of SmS			
М	at%Sm	at%S	$SmS_x$	at%Sm	at%S	$SmS_x$	
1:1	50	50	1	49.8	50.2	1.01	
1:1.11	50.9	49.1	0.96	49.9	50.1	1.00	
1:1.5	53.8	46.2	0.86	50.1	49.9	1.00	
1:1.8	55.9	44.1	0.79	50.1	49.9	1.00	
1:2.0	57.1	42.9	0.75	53.9	46.1	0.86	
1:3.0	62.5	37.5	0.60	52.3	47.7	0.91	
1:3.5	64.7	35.3	0.55	52.1	47.9	0.92	

Table 4.1 Nominal and actual compositions of synthetic SmS<sub>x</sub>

Figure 4.3 shows typical SEM micrographs of synthetic  $SmS_x$  powders at 1273 K for 3 hr. The synthetic  $SmS_x$  powder has large particle and reunited together because solid phase sintering happens. The added Sm content has no influence on the particle size of synthetic  $SmS_x$ .



Fig. 4.3 SEM micrographs of synthetic SmS<sub>x</sub> powder Reaction process of the formation of SmS<sub>x</sub> was analyzed by the thermodynamic data as shown in Fig. 4.4. There is no thermodynamic data for SmH<sub>3</sub>, so the standard free energy change for the thermal decomposition reaction of SmH<sub>3</sub> in equation (1) cannot be calculated. However, thermodynamic data of LaH<sub>2</sub>, CeH<sub>2</sub> and PrH<sub>2</sub> show the decomposition reaction of the Gibbs free energy change from positive to negative following with increasing temperature and atomic number. According to the variation of vacuum degree during the experiment, the decomposition of SmH<sub>3</sub> began at about 773K and completed at 1073K. The obtained Sm with higher activity can react with Sm<sub>2</sub>S<sub>3</sub> to fabricate SmS as shown in the equation (3).

In this study, maintaining a high vacuum was very important throughout the process of the reaction. The oxidation reaction of metal samarium proceeded to be easier in the way of equation (4). The standard free energy change is negative, so this reaction is easy to advance the right in any of the temperature. Also, the reaction between the product of  $Sm_2O_3$  in equation (4)  $Sm_2O_3$  and starting material of  $Sm_2S_3$  is believed to generate  $Sm_2O_2S$  as shown in the equation (5). The weak peak of  $Sm_2O_2S$  was easier to be occurred when the vacuum is not well. According to the standard free energy of the formation of  $Sm_2O_2S$ , equation (5) proceeded to be easy. If metal Sm was employed as Sm source for the preparation of SmS,  $Sm_2O_3$  layer on the surface of metal Sm easily led to trace  $Sm_2O_2S$  in the final product [129]. However, the hydrogen gas from the decomposition of  $Sm_3O_2S$ , but also can reduce trivalent Sm.

$$SmH_3(s) \rightarrow Sm(s) + 3/2H_2(s) \tag{1}$$

$$Sm(s) \rightarrow Sm(l)$$
 (2)

$$\operatorname{Sm}_2S_3(s) + \operatorname{Sm}(l) \to 3\operatorname{Sm}S(s)$$
 (3)

$$2Sm(l) + 3/2O_2(g) \rightarrow Sm_2O_3(s)$$
 (4)

$$1/2Sm_2S_3(s) + Sm_2O_3(s) \rightarrow 3/2Sm_2O_2S(s)$$
 (5)



Fig. 4.4 Gibbs free energy analysis of reaction process

## 4.3.2 Sintering of SmS<sub>x</sub> compacts

Figure 4.5 showed XRD results of the sintered  $SmS_x$  compacts from the annealed powder at 1373 K for 1 hr by SPS. Linear shrinkage curve of  $SmS_x$  compact suggested shrinkage of  $SmS_x$  started from 973 K and finished at about 1373 K. It is reasonable for the melting point of 2353 K. So,  $SmS_x$  was obtained only at 1373 K. Moreover, there is non-sintered at 1273K. A crack was observed in the sintered body with increasing the sintering temperature to 1473K and sintered  $SmS_x$  samples are easy to be cracked for high sintering temperature (above 1473 K). Compared with the results in Fig. 4.2, the lattice constant of  $SmS_x$  has no change before and after sintering. Finally, target composition of samarium rich samples  $SmS_{1.0}$ ,  $SmS_{0.857}$ , and  $SmS_{0.667}$  were conducted to evaluate the cross-sectional structure observation and thermoelectric properties.



Fig. 4.5 XRD of SmS<sub>x</sub> sintered at 1373 K for 1 hr Figure 4.6 showed SEM image of the sintered SmS<sub>x</sub> for the cross section of fracture surface. The sintered SmS<sub>x</sub> is entirely homogeneous and there is no obviously

preferred orientation. In addition, the particle size of the  $SmS_x$  grain becomes larger as samarium content increases. On the other hand, the brittle fracture is within the grain boundary and the existence of cleavage plane can explain the crack of sintered  $SmS_x$ .



Fig. 4.6 SEM micrograph of  $SmS_x$  compacts on the fracture surface 4.3.3 Electrical transport properties of  $SmS_x$  compacts

Figure 4.7 shows electrical resistivity  $\rho$  as a function of temperature for selected SmS<sub>x</sub> compacts. The  $\rho$  value of SmS<sub>x</sub> ( $0.86 \le x \le 1.07$ ) decreases as temperature increase, indicating it is semiconductor. The  $\rho$  value of SmS<sub>x</sub> ( $0.86 \le x \le 1.07$ ) show similar temperature dependence and the values are close to each other, indicating that electrical resistivity of SmS<sub>x</sub> does not have larger variation before Sm content reach the saturation in the solid solution. The electrical resistivities were dramatically

reduced as the Sm content increasing to 57.2 %, but slightly increased as reaction ratio increased to 3.5. In addition, electrical resistivity of  $SmS_x$  (0.55  $\leq x \leq$  0.75) first increased and then decreased. This should be attributed to the surplus of Sm. The residual Sm randomly distributed in the SmS matrix, which lead a markedly reduced electrical resistivity and the metallic behavior from 300 K to 450 K.



Fig. 4.7 Electrical conductivity  $\sigma$  for selected SmS<sub>x</sub> compacts

Temperature dependent Seebeck coefficients of  $SmS_x$  (0.55  $\le x \le 1.07$ ) compounds are plotted in Fig. 8. The Seebeck coefficient of  $SmS_x$  (0.55  $\le x \le 1.07$ ) is negative indicating that it is n-type semiconductor, which increased as the temperature rises. The magnitude of the absolute Seebeck coefficients values is distributed between 170 and 280  $\mu$ V·K<sup>-1</sup> and increases as samarium-rich content added in the target composition. The Seebeck coefficient of  $SmS_x$  (0.67  $\le x \le 1.07$ ) decreased with increasing temperature while Seebeck coefficient of  $SmS_x$  (0.55  $\le x \le 0.75$ ) showed weak temperature dependence. Seebeck coefficient first increased as Sm ratio increasing, saturate at  $SmS_{0.67}$ , then decreased as Sm ratio increasing (except the abnormal  $SmS_{0.75}$ ). The abnormal behavior of  $SmS_{0.75}$  should be attributed the actual composition deviate the nominal value too much, as also indicated by electrical resistivity.

Compared with chemical composition analysis of synthesized  $SmS_x$  as listed in Table 1, the actual chemical composition for the synthesized  $SmS_x$  ( $0.86 \le x \le 1.07$ ) was near stoichiometric and Seebeck coefficients of  $SmS_x$  ( $0.86 \le x \le 1.07$ ) present totally the increasing trend with the rising of temperature. The surplus Sm atoms which randomly distributed in the  $SmS_x$  (0.55  $\leq x \leq 0.75$ ) matrix occurred valence transitions and generated electrons. Due to the existences of these generated electrons, the variation of Seebeck coefficient show zigzag curves in Fig. 4.8.





Figure 9 shows power factor of synthetic  $SmS_x$  (0.55  $\le x \le 1.07$ ). In the whole, power factor of synthetic  $SmS_x$  increased with the Sm content. The abnormal behavior of  $SmS_{0.96}$  should be attributed the actual composition fluctuate. Power factor of synthetic  $SmS_{0.55}$ ,  $SmS_{0.6}$  and  $SmS_{0.67}$  were significantly increased, however, there is no obvious trend that can be observed as Sm content increasing to 64.7 %, suggesting power factor is sensitive to Sm ratio when reaction ratio is above 2. The optimized power factor was found to be 1500  $\mu$ W·K<sup>-2</sup>·m<sup>-1</sup> for  $SmS_{0.60}$  and  $SmS_{0.75}$  between 323 ~ 623 K. This value is comparable to that of reported power factor of composition of  $SmS_{0.965}$  (1400  $\mu$ W·K<sup>-2</sup>·m<sup>-1</sup> at 1000 K).



Fig. 4.9 Power factor of  $SmS_x$  ( $0.55 \le x \le 1.07$ ) compacts clusions

## **4.4 Conclusions**

The stoichiometry  $Sm_3S_4$  has been generated when the content of samarium in starting material was less than 50 %. Semiconductor SmS is generated after annealing and sintering. Since the shrinkage was completed around 1400 K according to the shrinkage curve, sintering of SmS was carried out at 1373 K to obtain an uncrack sintered compact. The Seebeck coefficient of  $SmS_x$  ( $0.67 \le x \le 1.07$ ) lessens with the rises of temperature and Sm content. The electrical resistivity of  $SmS_{0.75}$  had a clearly reduction following the increase of  $SmH_3$  content. Power factor of the obtained samples was about the same level as those in the previous reports at 323 ~ 623 K.

## **Chapter 5 Conclusions**

Yb<sub>2</sub>O<sub>3</sub> powders with different characters were employed to research the influence of particle size and specific surface area on the synthesis of Yb<sub>2</sub>S<sub>3</sub>. The main conclusions are as follows: (1) High sulfurization temperature (1000 °C) and small particle size are necessary for preparation of single hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub>. Larger specific surface area (50 m<sup>2</sup>/g) of Yb<sub>2</sub>O<sub>3</sub> is better for fabrication of orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> at low temperature of 600 °C for 8 hr. However, single Yb<sub>2</sub>S<sub>3</sub> cannot be obtained if specific surface area of Yb<sub>2</sub>O<sub>3</sub> is less than 2 m<sup>2</sup>/g and particle size is larger than 5 µm. (2) Sulfurization time (0.5 hr) tends to decrease with increasing temperature (1050 °C). CS<sub>2</sub> gas flow rate does not only influence the sulfurization efficiency and products, but also control the impurity content. Particle sizes of synthetic orthorhombic  $\eta$ -Yb<sub>2</sub>S<sub>3</sub> and hexagonal  $\epsilon$ -Yb<sub>2</sub>S<sub>3</sub> are dependent on sulfurization condition and impurity content. (3) Heavy Ln<sub>2</sub>O<sub>3</sub> are comparatively difficult to be sulfurized than light Ln<sub>2</sub>O<sub>3</sub>. To modify characters of Ln<sub>2</sub>O<sub>3</sub> is an effective step for preparation of Ln<sub>2</sub>S<sub>3</sub>.

Hexagonal  $\varepsilon$ -Yb<sub>2</sub>S<sub>3</sub> was synthesized at above 1000°C by sulfurizing its oxide with CS<sub>2</sub> gas. The synthetic Yb<sub>2</sub>S<sub>3</sub> is more stable in sulfur-rich atmosphere than argon gas or vacuum at about 1000°C. Yb<sub>2</sub>S<sub>3</sub> phase transformed to Yb<sub>3</sub>S<sub>4</sub> phase (1000 °C for 3 hr or 1200 °C for 1 hr) or YbS phase (1500 °C for 3 hr) during annealing. Yb<sub>2</sub>S<sub>3</sub> had better phase stability below 1400 °C with spark plasma sintering. The phase stability of Yb<sub>2</sub>S<sub>3</sub> probably depended on the sulfur vapor pressure.

Single-phase Eu<sub>3</sub>S<sub>4</sub> could be obtained via sulfurization of Eu<sub>2</sub>O<sub>3</sub> using CS<sub>2</sub> gas at 773 K, independent of the sulfurization time. Single-phase EuS was also obtained for sulfurization temperature of 1073 K or higher, independent of the sulfurization time. Single-phase EuS could be obtained at sulfurization temperatures of 973 or 1073 K when the corresponding sulfurization times were 8 and 3 hr, respectively. Although the specific surface area of the product decreased as the sulfurization temperature increased, the decrease in the specific surface area was minimal, accompanied by cubic expansion, when the phase transformation from Eu<sub>3</sub>S<sub>4</sub> to EuS occurred. In the evaluation of the effect of heat treatment on the phase transformation from Eu<sub>3</sub>S<sub>4</sub> to EuS at a fixed heat treatment time of 1 hr, it was found that heat treatment at 973 K or higher in a CS<sub>2</sub>/Ar atmosphere, at 1073 K or higher in an Ar atmosphere, and at 873 K or higher in a vacuum atmosphere, yielded single-phase EuS. Heat treatment of  $Eu_3S_4$  powder generated a small amount of  $Eu_2O_2S$  because of impurity oxygen in the  $Eu_3S_4$  powder and oxygen in the vacuum atmosphere. When heat treatment was performed at high temperatures in the CS<sub>2</sub>/Ar atmosphere, the formation of  $Eu_2O_2S$  could be inhibited.

The stoichiometry  $Sm_3S_4$  has been generated when the content of samarium in starting material was less than 50%. Semiconductor SmS is generated after annealing and sintering. Since the shrinkage was completed around 1400K according to the shrinkage curve, sintering of SmS was carried out at 1373K to obtain an uncrack sintered compact. The Seebeck coefficient of  $SmS_x$  (0.67<x<1.07) lessens with the rises of temperature and Sm content. The electrical resistivity of  $SmS_{0.75}$  had a clearly reduction following the increase of  $SmH_3$  content. Power factor the obtained samples was about the same level as those in the previous reports at 323 ~ 623K.
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# **List of Publications**

## **Journal Paper:**

(1) **Li Liang**, Hirai Shinji, Yuan Haibin, "Influences of  $Yb_2O_3$  characters and sulfurization conditions on the preparation of  $Yb_2S_3$ ", Journal of Alloys and Compounds, Vol. 618, No. 5, pp. 742-749, 2015.

(2) **Liang Li**, Shinji Hirai, Haibin Yuan, Eiji Nakamura, "Synthesis of ytterbium sulfides by the sulfurization and heat treatment", Key Engineering Materials, Vol. 655, pp. 224-229, 2015.

(3) **Li Liang**, Shinji Hirai, Eiji Nakamura, Haibin Yuan, "Influences of Eu<sub>2</sub>O<sub>3</sub> characters and sulfurization conditions on the preparation of EuS and its large magnetocaloric effect", Journal of Alloys and Compounds, Vol. 687, pp. 413-420, 2016.

(4) **Li Liang**, Shinji Hirai, Eiji Nakamura, Haibin Yuan, "Synthesis of europium sulfides by CS<sub>2</sub> sulfurization and heat treatment", MRS Advances, DOI: <u>http://dx.doi.org/10.1557</u>/adv.2016.346.

(5) Li Liang, Shinji Hirai, Yohei Tasaki, "Synthesis and sintering of samarium rich  $SmS_x$  and its electrical property", Journal of Rare Earths, (Accepted).

### **International Proceedings:**

(1) Liang Li, Shinji Hirai, et. al, "Synthesis of valence-fluctuation rare-earth monosulfides and their specific heat characteristics at very low temperatures, 2015 MRS Fall meeting, 2015.12.3; (Poster),Boston, USA.

(2) **Liang Li**, Shinji Hirai, et. al, "Synthesis of high-purity EuS prepared by  $CS_2$  sulfurization and heat treatments, 9th international conference on f-elements, 2015.9.7(Poster), Oxford, UK.

(3) **Liang Li**, Shinji Hirai, et. al, "Synthesis and phase transformation of europium sulfides prepared by CS<sub>2</sub> sulfurization", 3rd International Doctoral Student Symposium on Material Science, 2015.2.26; (Oral), Sapporo, Hokkaido, Japan.

(4) **Liang Li**, Shinji Hirai, Haibin Yuan, "Synthesis of ytterbium sulfides by the sulfurization and heat treatment", 5th International Congress Ceramics, 2014.8.20; (Oral) Beijing, China.

### **Proceedings of Local Presentation:**

(1) **Liang Li**, Shinji Hirai, et. al, "Synthesis and sintering of polycrystalline EuS and its magnetocaloric effect at low temperature", Muroran-IT Rare Earth Workshop2016, 2016.6.11, Rusutsu.

(2) **Liang Li**, Shinji Hirai, et. al, "Synthesis of europium sulfides by CS<sub>2</sub> gas sulfurization and their phase transformation",資源.素材(春)2015.3.29,千葉.

(3) 李良,葛谷俊博,平井伸治, "Yb<sub>2</sub>O<sub>3</sub>の CS<sub>2</sub>ガス硫化と熱処理によるイッテルビウム硫化物 の合成",資源·素材 2014.9.15, 熊本.

(4) **李良**, 葛谷俊博, 平井伸治, "Yb<sub>2</sub>O<sub>3</sub>の CS<sub>2</sub>ガス硫化と熱処理による YbS の合成",日本金 属学会北海道支部,2014.7.28, 札幌.

(5) 朝倉貴一,Fan Haotian,Liang Li,平井伸治,中村英次,太田道広,葛谷俊博, "反応焼結法によるテトラヘドライト型 Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>焼結体の作製", 資源·素材(春)2015. 3.29,千葉.

(6) 金澤昌俊,李良,葛谷俊博,関根ちひろ,平井伸治,"重希土類硫化物 Ln<sub>2</sub>S<sub>3</sub>の圧力ー温度相 図",第1回物構研サイエンスフェスタ,2013.3, つくば.

(7) 金澤昌俊,李良,葛谷俊博,関根ちひろ,平井伸治,"重希土類硫化物 Ln<sub>2</sub>S<sub>3</sub>の高温高圧合成 II",第 54回高圧討論会,2013.11,新潟.

(8) 金澤昌俊,李良,葛谷俊博,関根ちひろ,平井伸治,"重希土類硫化物 Ln<sub>2</sub>S<sub>3</sub>の高温高圧合成", 第 53 回高圧討論会,2012.11, 大阪.

(9) 松本宏一,村山大樹,裏雄太郎,宇治山崇,**李良**,平井伸治,中村英次,"希土類硫化物 EuS の磁 気熱量効果", 2015 年度秋季低温工学・超電導学会, 2015.12.2-4, 神戸.