Synthesis of Sc sulfides by CS_2 sulfurization

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Abstract

Scandium sulfides were synthesized from its stable oxide, Sc_2O_3, using CS_2 gas. Suitable temperature and time for synthesis were examined experimentally using a constant flow rate of gas mixture of Ar and CS_2. The high rate of evaporation from liquid CS_2 enhanced formation and stoichiometry of sulfides, and eliminated impurity carbon. Most of parts in the sample were converted to Sc_2S_3 at 1473 K for 7.2 ks, and a transient phase of Sc_2O_2S was often synthesized after a prolonged time under certain oxygen and sulfur potentials.

Keywords: synthesis of scandium sulfides, CS_2 gas sulfurization, rare earth compounds, gas-solid reactions

1. Introduction

In recent years, non-ferrous metallic sulfides have attracted strong attention in various fields, even if they do not exist as oxide ores in the nature. The sulfides of lithium and titanium have been studied intensively because of their applications as solid electrolytes in solid state batteries [1,2]. TiS_2 and rare earth sulfides exhibit excellent thermoelectric properties such as low thermal conductivity and high electric conductivity [3-5], and the materials explore as thermoelectric elements has been intensively conducted [5-9]. In this study, we focused on scandium sulfide, which contains one of the rare earth elements.

Refining of metal sulfides in molten salts has been recently developed by the authors as an efficient method for producing metallic powders without oxygen contamination [10-15]. For example, an industrial grade Ti metal powder has been successfully produced from its oxide, TiO_2, via titanium sulfides, (i.e. $Ti_{2.45}S_4$ and TiS_2) [14, 15]. Thermodynamically, it is impossible to reduce Sc_2O_3, the most stable metal oxide [16], to metallic Sc directly by Ca because of its strongest affinity for oxygen [17-19]. However, thermodynamic data indicate that the calciothermic reduction of scandium sulfide (Sc_2S_3) may be possible/viable which is due to the different stability of oxide and sulfides of scandium.

Several methods for synthesis of scandium sulfide from the oxide have been known [20-22]. The first method is direct reaction between metallic scandium and elemental sulfur in an encapsulated quartz ampoule [20]. In this method a highly pure sulfide of scandium can be synthesized, although

45 scandium metal powder is extremely expensive, and the amount of obtained sulfide is limited.
46 Therefore, it is desirable to synthesis Sc_2S_3 directly from Sc_2O_3 rather than serving an expensive
47 scandium metal as a starting material.

48 The second method is sulfurization of Sc_2O_3 in the gas flow of hydrogen sulfide (H_2S) using a
49 graphite crucible at 1823 K [21].

50 $$Sc_2O_3 + 3\ H_2S(g) = Sc + 3\ H_2O(g), \quad \Delta G^0(1) = 272.3\ \text{kJ/mol at 1823 K [16]} \qquad (1)$$

51 $\Delta G^0(1)$ is Gibbs free energy change for the reaction (1). Indeed, the reaction between Sc_2O_3 and H_2S
52 gas is thermodynamically unfavorable [16] and a contribution of carbon may be required to obtain
53 Sc_2S_3 as product.

54 $$Sc_2O_3 + 3\ H_2S(g) + 3\ C = Sc_2S_3 + 3\ H_2(g) + 3\ CO(g)$$

55 $$\Delta G^0(2) = -298.8\ \text{kJ/mol at 1823 K [16]} \qquad (2)$$

56 When both carbon and gaseous H_2S are simultaneously used in the process, the sulfurization can
57 occur because strong reducibility of carbon is preferentially utilized. This may, however, decrease
58 the reaction efficiency by large amount of H_2S consumption.

59 The sulfurization of Sc_2O_3 using gas mixture of Cl_2 and S_2Cl_2 was briefly reported [22], but the
60 coexisted $ScCl_3$ should be additionally converted using H_2S gas and sublimation to obtain pure Sc_2S_3.
61 No additional report has been found since 1930.

62 On the other hand, CS_2 gas can be easily used for sulfurization of oxides. It has been reported

63 that stable oxides such as TiO_2 can be converted to TiS_2 in CS_2 gas [5,13,15]. Silicon sulfide and rare
64 earth sulfides have been also successfully synthesized in a CS_2 gas atmosphere [23-26]. CS_2 gas can
65 serve carbon and sulfur simultaneously with a stoichiometric molar ratio, and react with Sc_2O_3 due
66 to its strong thermochemical reducibility and sulfurization ability. The overall sulfurization reaction
67 can be written apparently as reaction (3),

68 $$Sc_2O_3 + 3/2\ CS_2(g) = Sc_2S_3 + 3/2\ S_2(g)$$

69 $$\Delta G^0(3) = -42.8\ \text{kJ/mol at 1473 K, and -40.5 kJ/mol at 1273 K [16]} \quad (3)$$

70 where an inert gas such as Ar is used to transport the vaporized sulfurizing agent (CS_2 gas) into the
71 reaction vessel. This can be performed by injecting an inert gas into liquid CS_2 and vaporizing CS_2 at
72 room temperature, for example.

73 The boiling point of CS_2 is as low as 315 K [16], and it can be easily handled and fed into the
74 reaction vessel rather than elemental sulfur which is solid at ambient temperature. It is worth noting
75 that the melting temperature of sulfur is 388.4 K [16], and that the evaporation requires an additional
76 furnace to keep a constant temperature above 473 K [17]. Moreover, the excess CS_2 gas can be
77 collected by cooling due to its very low boiling point. The CS_2 gas is commonly used as a solvent for
78 organic materials. A constant supply of CS_2 at a reasonable cost is desired for the sulfurization
79 process (reaction (3)). No literature survey is available on the preparation of Sc_2S_3 from Sc_2O_3 as far
80 as the authors are aware.

Sc_2S_3 has a potential as sulfide-based solid electrolyte for fuel cells and as new thermoelectric materials, similar to the other rare-earth sulfides [1-9]. Because Sc_2S_3 has a characteristically bright yellow color, it can be expected to be used as a yellow pigment [20-22] and as n-type semi-conductor [20] for optical application. The authors are expecting that Sc_2S_3 can be a starting material for scandium metal production.

The purpose of this paper is to synthesize Sc_2S_3 from Sc_2O_3 by employing CS_2 gas as powerful sulfurizing agent. This paper studies the optimal evaporation temperature of CS_2 gas as well as sulfurization temperature to form the single phase of Sc_2S_3. Morphology of the sulfurized samples was also rigorously investigated.

2. Experimental procedure

2.1 Materials and experimental setup

Sc_2O_3 powder with the purity of 99.9% was supplied by Sumitomo Metal Mining Co., Ltd. Fig. 1 shows the experimental setup [13]. The vapor pressure of volatile CS_2 (99.99%, Wako Chemical Co.) is so high even at room temperature that it can be fed to the hot reaction zone by a constant flow of Ar gas (>99.9998%, 20 mL/min.). The evaporation temperature of CS_2 gas was kept constant by water bath. A dense alumina tube (24 mm ID) was used as a reaction tube, and unreacted exhaust gas was trapped by using 1.0 M NaOH solution. In the sulfurization experiment, 0.25 g of the Sc_2O_3 was

weighted and filled into an alumina boat (>99.5%, 14mm wide, 100 mm long). The sample was heated in vacuum up to the sulfurization temperature. Then, a mixture of Ar and CS_2 gas was served for the sulfurization. The sulfurization temperature was varied in the range between 1273 K and 1473 K, and both the heating and cooling rates were 10 K/min. After cooling, the mass changes of the samples were precisely measured to estimate the sulfurization degree of the samples.

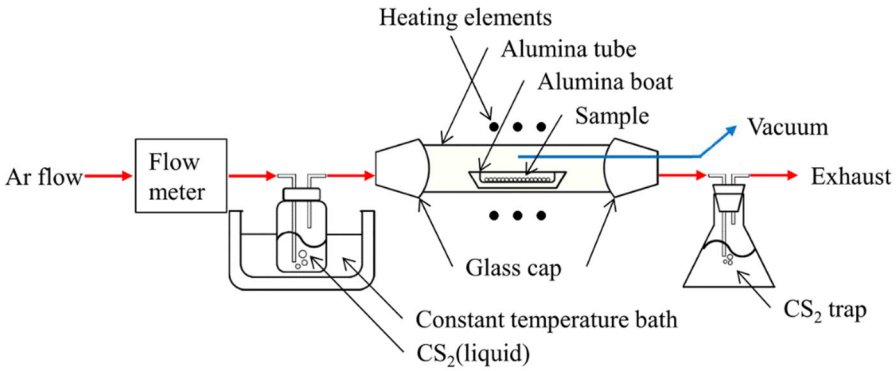


Fig.1 A schematic illustration of the experimental setup.

2.2 Characterization

The samples were analyzed by X-ray diffraction (XRD) measurement using Philips X'Pert Pro, Cu-K_α). The morphology of as-received and the sulfides of scandium were characterized by scanning electron microscopy (SEM, JSM-6510LA). The carbon and sulfur concentrations in the obtained samples were quantitatively analyzed by the IR spectroscopic analysis of CO_2 and SO_2 gases, respectively, using LECO CS-600. The oxygen concentration was also analyzed by the inert-gas fusion method using LECO TC-600.

3. Results and discussion

3.1 Optimal reaction temperature and time

The optimal sulfurization temperature and time suitable for formation of Sc_2S_3 from Sc_2O_3 were examined, where the evaporation temperature of CS_2 was set constant at 273 K. Fig. 2 shows the mass change (Δm) of the sulfurized samples at temperatures ranged from 1273 K and 1473 K for 7.2 ks. At 1473 K, the mass change (Δm) was close to the ideal mass gain from Sc_2O_3 to Sc_2S_3. It is noted that the sufficient amount of CS_2 was supplied in the experiment, the amount of sulfur in the consumed CS_2 gas in 7.2 ks was 21.5 times more that the stoichiometric sulfur required for formation of Sc_2S_3 in conversion of Sc_2O_3 perfectly to Sc_2S_3 at the operating conditions.

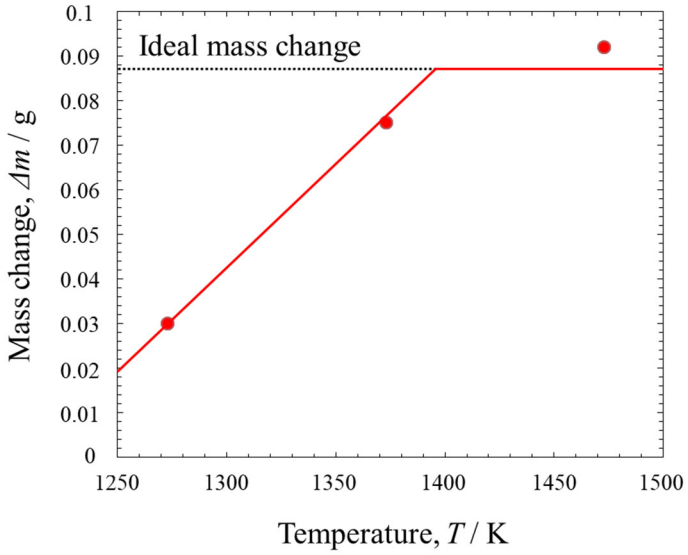


Fig.2 Mass change after CS_2 gas sulfurization for 7.2 ks.

Fig.3 shows the time dependency of mass changes of the samples. The mass changes were smaller than the ideal value at all the temperatures when the sulfurization time was as short as 1.8 ks.

At 1273 K, the mass gradually increased as the time prolonged, however, the mass changes did not approach the ideal value for a complete conversion, and it approached about a 1/3 value of the expected stoichiometry, Sc_2S_3. At 1373 K, the mass did not arrive to the ideal mass for the shorter time such as 3.6 ks and 7.2 ks, but the sample reacted for 10.8 ks showed the ideal mass gain. At 1473 K, the mass change was close to ideal value of Sc_2S_3 even after 3.6 ks, and did not increase after 3.6 ks. Thus the sulfurization occurred at a fairly fast rate and it related strongly with the operation temperature.

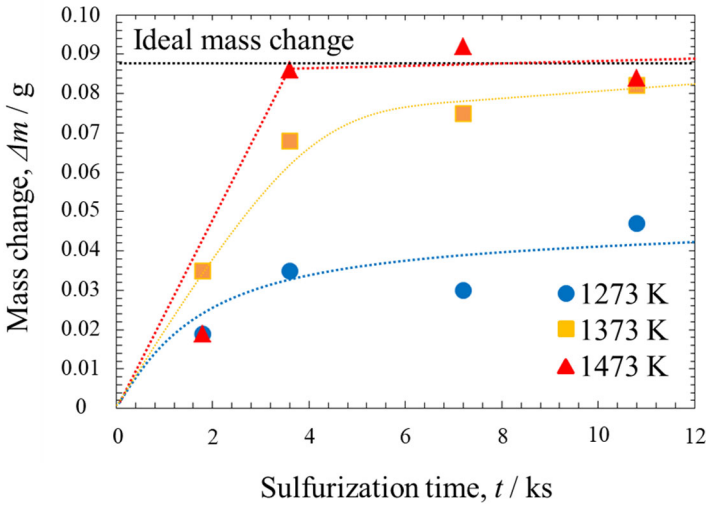


Fig.3 Mass change after CS_2 gas sulfurization.

Fig. 4 shows the appearance of the sample after sulfurization at 1473 K for 7.2 ks. The color as shown in Fig.4(a) was bright yellow and slightly sintered, although the starting oxide, Sc_2O_3, is white and powdery. The yellow product was easily pulverized by soft finger touching.

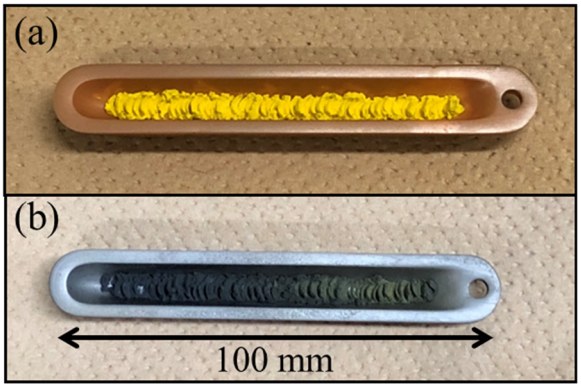
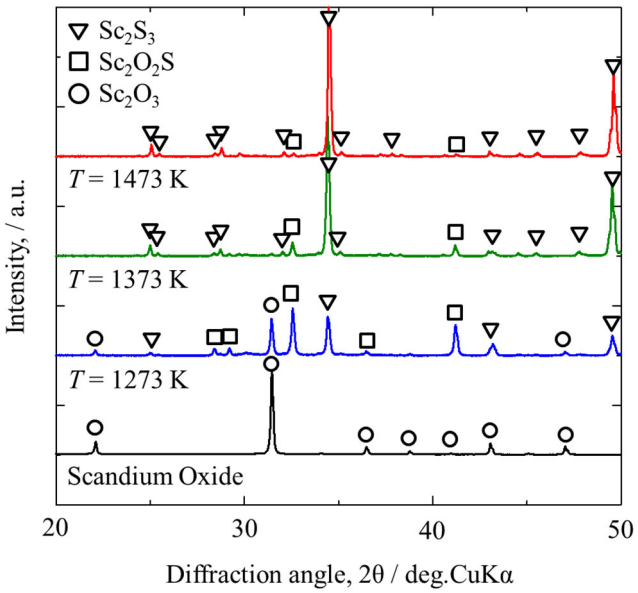


Fig.4 Apparent view of sulfurized sample at 1473 K for 7.2 ks. CS_2 liquid was hold at 273 K (a), and 313 K (b).

Fig.5 shows the XRD patterns of as-received and the sulfurized samples at various temperatures. After sulfurization for 7.2 ks at the lowest investigated temperature of about 273 K, Sc_2O_3 (ICSD No. 01-073-1691)[27], Sc_2O_2S (ICSD No. 01-070-1251)[28-30] and Sc_2S_3 (ICSD No. 01-073-0451) [21] were identified in the samples, indicating the formation of Sc_2S_3 through an intermediate oxysulfide phase. By increasing the reaction temperature to above 1373 K, the intensities of the XRD peaks associated to oxide and oxysulfide significantly decreased. Further increasing the temperature to 1473 K resulted in formation of the sulfide of Sc_2S_3 with a small amount of Sc_2O_2S. A faint amount of Sc2O2S was still found in the sample prepared at 1473 K for 7.2 ks, although the major phase was Sc2S3 and any diffraction peaks of Sc2O3 was not detected. Thus, the sample synthesized at 1473 K could be considered as nearly single phase of Sc_2S_3.



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162 Fig. 5 X-ray diffraction patterns of the samples sulfurized at various temperatures for 7.2 ks.

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164 In addition, the sulfurization experiments were conducted at 1373 K for various periods ranged

165 from 1.8 ks to 7.2 ks. Fig.6 shows the time dependency of phase transition by XRD patterns at 1373

166 K. The sample prepared for 1.8 ks contained three phases including Sc_2O_3, Sc_2O_2S and Sc_2S_3. After

167 sulfurization for 3.6 ks, the intensities of the XRD peaks of Sc_2O_3 and Sc_2O_2S decreased and Sc_2S_3

168 became the dominant phase in the product. The XRD patterns of the samples synthesized at 1373 K

169 in 3.6 ks and 7.2 ks were almost similar, and a slight decrease in intensity of Sc_2O_2S peaks was

170 observed. The peaks related to Sc_2O_3 were completely disappeared after sulfurization for 3.6 ks and

171 7.2 ks. This indicates that Sc_2S_3 could be synthesized at shorter times.

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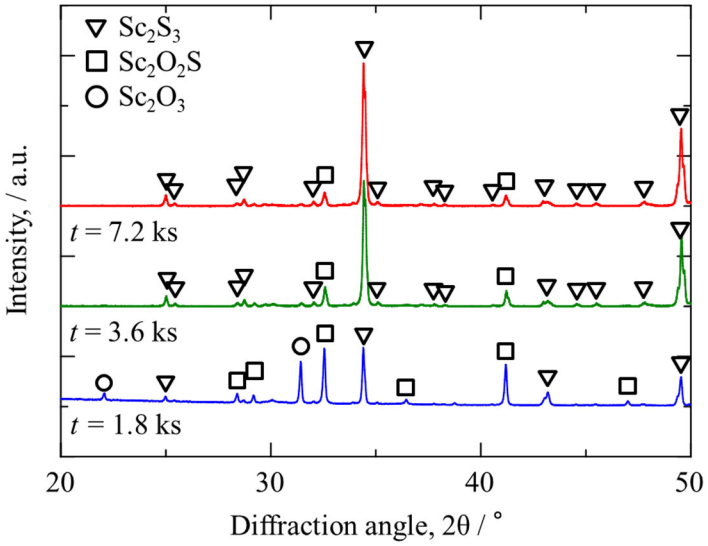

Fig.6 X-ray diffraction patterns of the samples sulfurized at 1373 K.

These phase identifications indicated that the sulfurization of Sc_2O_3 (reaction (3)) proceeds through the formation of an intermediate oxysulfide, Sc_2O_2S, that may be explained as follows:

$$Sc_2O_3 + 1/2\ CS_2(g) = Sc_2O_2S + 1/2\ CO_2(g), \quad (4)$$

$$Sc_2O_2S + CS_2(g) = Sc_2S_3 + CO_2(g), \quad (5)$$

Apparently, the replacement of one atom of oxygen in the oxide lattice by sulfur occurs, and the crystalline oxysulfide of Sc_2O_2S was then formed. Further substitution of oxygen atoms in Sc_2O_2S by sulfur results in formation of the most stable sulfide, Sc_2S_3. It is noted that only CO_2 gas is considered in the reactions (4) and (26). CO gas can be also considered in the parallel reactions as,

$$Sc_2O_3 + CS_2(g) = Sc_2O_2S + CO(g) + 1/2\ S_2(g) \quad (6)$$

$$Sc_2O_2S + 2\ CS_2(g) = Sc_2S_3 + 2\ CO(g) + S_2(g) \quad (7)$$

The experimental determination of the concentrations of CO and CO_2 in the gaseous phase is not

188 easy due to the presence of S_2 and the residual CS_2 gases, although it is thermodynamically possible

189 to consider simultaneous formation of CO and CO_2 gases in the reactions (4) – (7).

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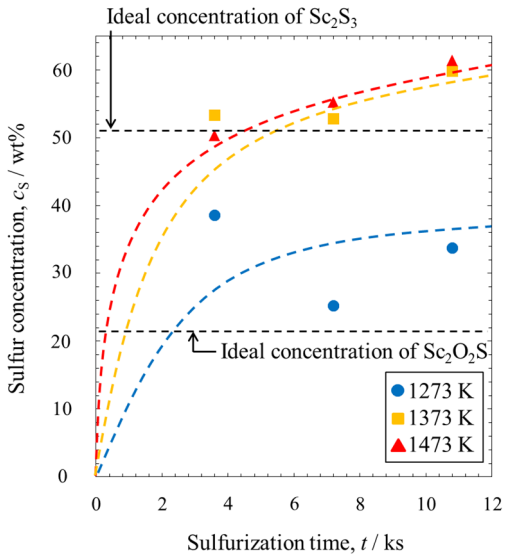

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193 Fig.7 Sulfur content of the sulfurized samples.

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195 The sulfur contents of the obtained samples were quantitatively analyzed as shown in Fig.7. It

196 should be noted that the stoichiometric Sc_2S_3 contains 51.7 wt%S, however, the highest sulfur

197 content of the sample obtained at 1273 K was about 40 wt%S, which is less than the stoichiometric

198 sulfur content of Sc_2S_3. The sulfur concentration of the samples synthesized at 1373 and 1473 K

199 were as high as 51.7 wt%S, even after a short reaction time such as 3.6 ks. The sulfur content of the

200 samples increased as the reaction time became longer. The increase of sulfur content above the

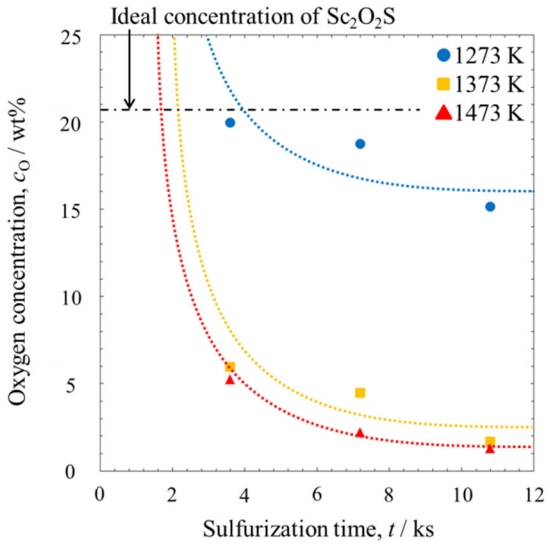
201 stoichiometry may reflect the non-stoichiometry in Sc_2S_3. The deposition of sulfur vapor on the

202 sample surface during cooling also increases the sample weight, because S_2 gas generates as the

203 reactions (6) and (7). It is certain that the excess amount of CS_2 gas caused the yellow deposition of

204 solid sulfur at the cold position of the downstream in the reaction tube.

205



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208 Fig.8 The residual oxygen content of the sulfurized samples.

209

210 Fig. 8 shows the residual oxygen of the sulfurized samples analyzed by LECO method. Note that

211 the oxygen concentrations in the stoichiometric oxide Sc_2O_3 and the oxysulfide Sc_2O_2S are 34.80

212 wt% and 20.79 wt%, respectively. The oxygen level of the samples sulfurized at 1273 K was very

213 high, while those at 1373 and 1473 K decreased to a low level. The oxygen concentration at 1473 K

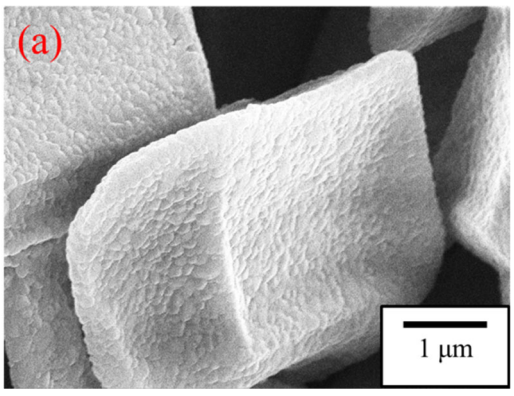
214 for 10.8 ks was analyzed as 1.31 wt%O as the lowest content. This means that the sulfurization

215 behavior significantly changed at a critical temperature between 1273 K and 1373K.

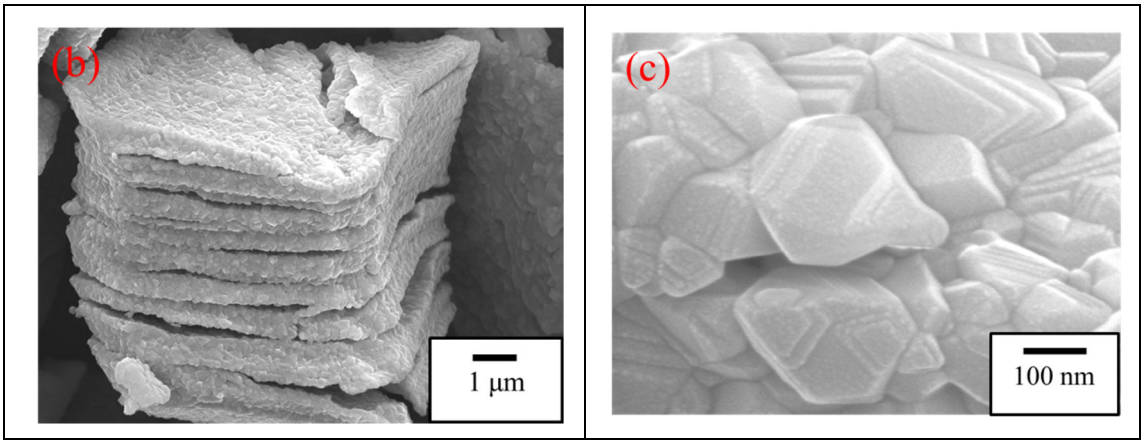
216

3.2 Microstructural characterization of the products

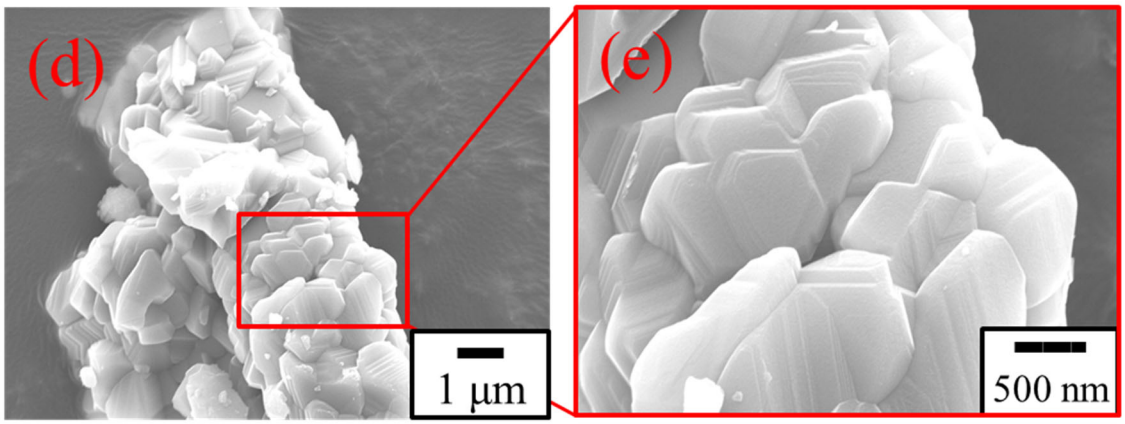
Fig. 9 shows the morphology of as-received oxide and the synthesized samples. As shown in Fig. 9(a), the raw material (Sc_2O_3) contained larger grains of about 4 μm and the finer particles of about 0.1 μm. These oxide particles were then sulfurized at 1273 K for 7.2 ks. Many cracks were formed in all the particles as shown in Fig. 9(b), which could be due to lattice mis-fitting between oxide and oxysulfide. EDX analysis showed the homogeneous distribution of sulfur and oxygen in all the particles. The oxysulfide particles were formed in hexagonal shape plates as shown in Fig. 9(c). Fig. 9(d) shows the morphology of the sulfide sample prepared at 1473 K for 7.2 ks. It consists of hexagonal grains, and they looks to grow toward the cylindrical directions accompanying with non-uniform branches. FE-SEM micrograph of the particles at higher magnification is shown in Fig. 9(e) in which the interconnected hexagonal plates of Sc_2S_3 with particle size of about 50 – 100 nm can be obviously seen.



(a)



(b) (c)



(d) (e)

Fig. 9 SEM images of (a) as-received scandium oxide and the synthesized sulfides at 1273 K (b, c), and 1473 K (d, e) for 10.8 ks.

3.3 Evaporation temperature of CS_2

Figures 10 and 11 show the mass changes and the oxygen concentration of the samples prepared at various conditions, respectively. Sulfurization of the samples was conducted at various temperatures for 7.2 ks, where the evaporation temperature of CS_2 liquid was varied. As the temperature of CS_2 liquid increases, the equilibrium vapor pressure is the higher [16], and the large amount of CS_2 gas is supplied into the hot zone of the furnace. The mass changes of the samples

increased due to the substitution of oxygen atoms by sulfur. The residual oxygen also changed as the temperature of CS_2 liquid varied, as shown in Fig.11.

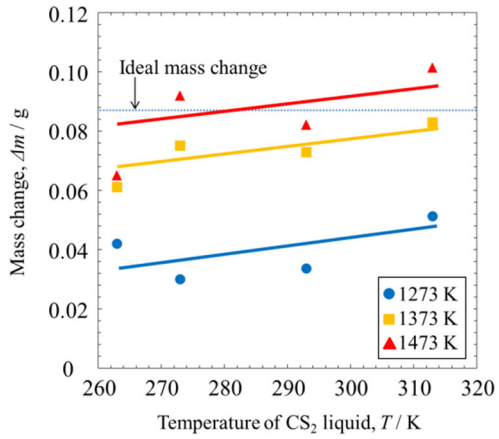


Fig.10 Mass change of sulfurized samples for 7.2 ks at various CS_2 evaporation temperatures.

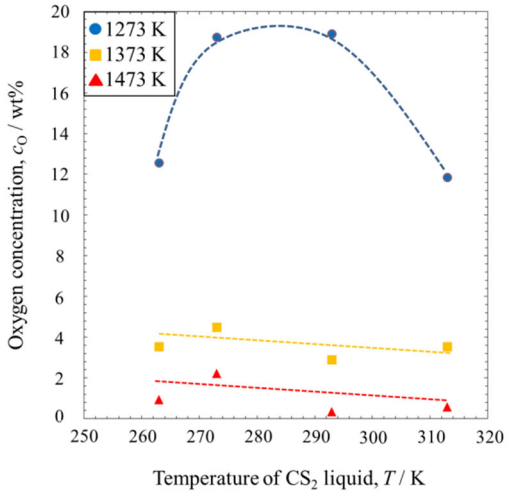


Fig. 11 Oxygen concentration of the sulfurized samples for 7.2 ks at various CS_2 evaporation temperatures.

When CS_2 gas is in equilibrium with its pure liquid as given in eq. (8), its vapor pressure can be thermodynamically determined as a function of temperature as written in eq. (9). The standard Gibbs

free energy change for the reaction (8), $\Delta G^0(8)$ [16], is used to evaluate the vapor pressure of CS_2, P_{CS2}, as shown in Fig. 12. The CS_2 gas at P_{CS2} was supplied to the reaction zone and it was apparently reacted with Sc_2O_3 to form Sc_2S_3 (reaction (3)), although it consisted of two stepwise reactions, (2)-(5).

$$CS_2(l) = CS_2(g) \quad (8)$$

$$P_{CS_2} = \exp\left(\frac{-\Delta G^0(8)}{RT}\right) \quad (9)$$

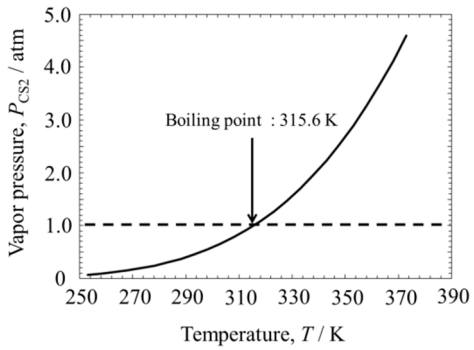


Fig.12 Vapor pressure of CS_2 vs evaporation temperature [16].

When the higher P_{CS2} is given by increasing the evaporation temperature of CS_2 liquid, the sulfurization can be thermodynamically enhanced. Assuming the coexistence of pure Sc_2O_3 and pure Sc_2S_3 as represented in reaction (3), the Gibbs free energy change of sulfurization, $\Delta G(3)$, can be written as eq. (10),

$$\Delta G(3) = \Delta G^0(3) + \frac{3}{2}RT\ln P_{CO_2} - \frac{3}{2}RT\ln P_{CS_2} \quad (10)$$

P_{CS2} can be given in eq.(9) as determined by the holding temperature of CS_2 liquid. On the other

hand, P_{CO2} is limited by the mass balance of charged amount of Sc_2O_3. Because CO_2 gas is diluted by carrier gas of Ar, P_{CO2} gradually decreases after completing the reaction. If we can assume P_{CO2} is nearly constant, the increase of holding temperature of CS_2 liquid increases P_{CS2}, and $\Delta G(3)$ can shift to the more negative value according to eq.(10). This enhancement of reaction lowers the residual oxygen content in the sulfide due to decomposition of oxide.

However, the specimens changed the color to black as shown in Fig. 4(b) when they were sulfurized by CS_2 gas evaporated at the holding temperature of CS_2 liquid as high as 313 K. Fig. 13 shows the residual carbon in the samples sulfurized for 7.2 ks. The black sample at 1473 K using CS_2 gas evaporated at 313 K was heavily contaminated with carbon (10.6 wt%C at the maximum), and the faint diffraction peaks matched with those of $Sc_{15}C_{19}$ (ICSD#00-038-0797) [30-32] among many Sc carbides [30-42], as shown in Fig. 14. It is noted that the chemical formula was reported earlier as $Sc_{15}C_{19}$ [30-32], and that it was revised as Sc_3C_4 by neutron diffraction measurements [39-42]. Hereafter we call $Sc_{15}C_{19}$ as Sc_3C_4. It was reported that the color of Sc_3C_4 crystal is a light gray with metallic luster, and the powdered sample is black [39]. The color changes are in agreement with this study.

Because the excess amount of CS_2 gas was fed to the sample, S_2 gas and Sc_3C_4 are produced from the decomposition of CS_2 gas.

$$3\ Sc_2S_3 + 8\ CS_2(g) = 2\ Sc_3C_4 + 25/2\ S_2(g) \quad (11)$$

The deposited carbon dissolves into sulfide, and a portion of carbon forms the carbide such as Sc_3C_4 when the amount of deposition exceeds the solubility of carbon. Because neither thermodynamic data on scandium carbides nor phase relationship among sulfides and carbides are available, the exact evaluation on eq. (11) can not be completed.

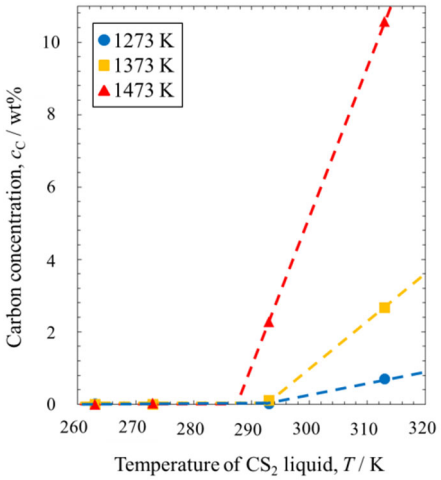


Fig.13 Carbon content of the samples prepared by evaporation of CS_2 at various temperatures.

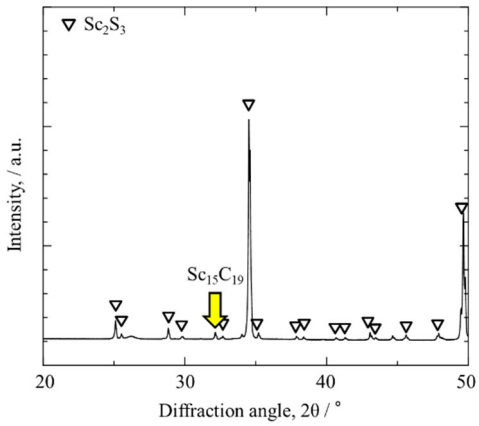


Fig.14 XRD pattern of sulfurized sample at 1473 K for 7.2 ks by using CS_2 gas evaporated at 313 K.

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305 Therefore, almost single phase of Sc_2S_3 with low oxygen concentration was successfully synthesized

306 at 1473 K by using CS_2 gas sulfurization technique. By controlling the feeding temperature of CS_2

307 liquid as low as 273 K, the carbon contamination could be minimized to 0.030 wt%C.

308

309 ## 3.4 Transient phase of Sc_2O_2S

310 The formation of oxysulfides (M_2O_2S type) have been reported for most of IIIa group elements

311 in the periodic table, *i.e.*, M=Y and rare earth metals from La to Lu [16, 26, 43-45]. The formation of

312 Sc_2O_2S was also reported in the mixture of Sc_2O_3 and Sc_2S_3 at 1773 K [28,29], by solidifying from

313 the melt at 1873 K [29], or by sulfurization of Sc_2O_3 in H_2S gas at 1823 K [21]. However, the

314 thermochemical data on Sc_2O_2S has not been reported and complied in the currently available

315 database [16]. The stability diagram of the oxides and sulfides in Sc-O-S ternary system was plotted

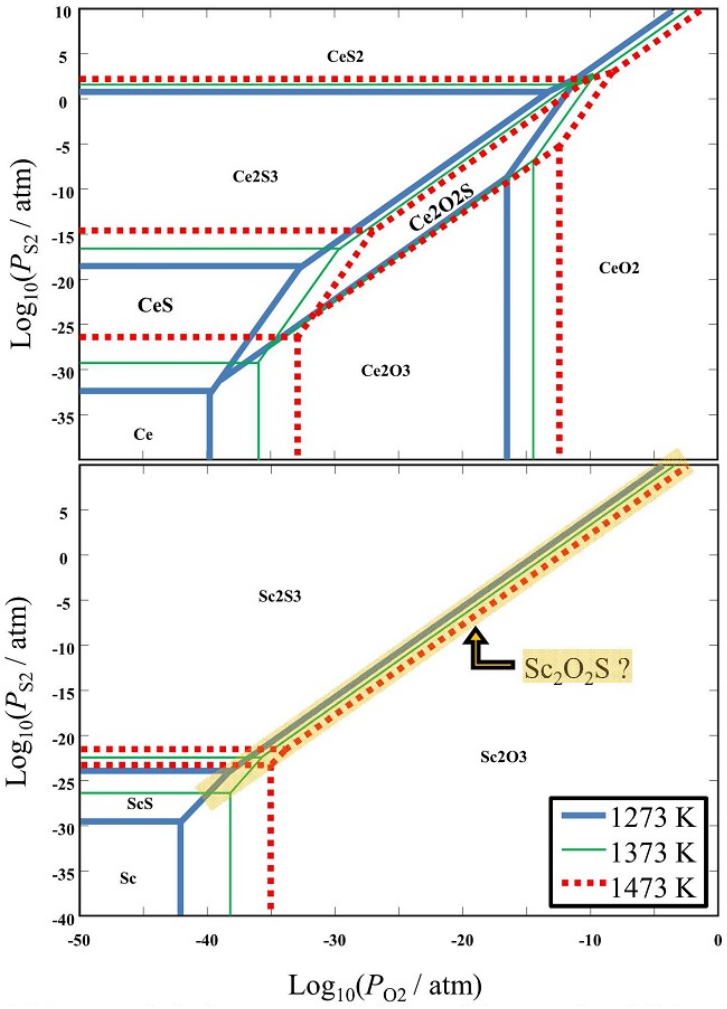
316 using only the available thermodynamic data [16]. As the first approach, the existence of Sc_2O_2S was

317 neglected at all the temperatures as shown in Fig. 15, which could be due to the lack of data. When

318 the temperature increases, the stable areas of metallic Sc and Sc_2S_3 expand, and those of ScS and

319 Sc_2O_3 shrink.

320



321

322 Fig.15 Potential diagram of the oxides and sulfides in the ternary Ce-O-S and Sc-O-S systems [16].

323

324 In synthesis of Sc_2S_3, the existence of Sc_2O_2S [28,29] was detected and ScS was never found in this

325 work. Because the stable region of ScS exists both at a very low partial pressure of sulfur (P_{S2}) and a

326 very low partial pressure of oxygen (P_{O2}) in Fig. 15, it is reasonable that ScS did not appear in a high

327 P_{S2} of CS_2 gas environment. If Sc_2O_2S was thermodynamically stable phase, the stable region of

328 Sc_2O_2S in Fig. 15 should exist at a boundary area between the regions of Sc_2S_3 and Sc_2O_3 (hatched

329 yellow area in Fig. 15). Hence, it is reasonable to refer to the stability region of Ce_2O_2S in the

330 Ce-O-S ternary system [16], where the phase boundaries between Ce_2O_3 and Ce_2O_2S and, between
331 Ce_2O_2S and Ce_2S_3 are parallel with that between Ce_2O_3 and Ce_2S_3. Therefore, the stable region of
332 Sc_2O_2S can be drawn in a similar way for Ce_2O_2S if the thermodynamic values can be obtained.
333 Because this work paid main attention in the synthesis of Sc_2S_3, the stability of Sc_2O_2S was not well
334 studied due to lack of thermodynamic data. It will be separately reported.
335

336 ## 4. Conclusion

337 This study experimentally examined the sulfurization of Sc_2O_3 by using CS_2 gas to obtain Sc_2S_3.
338 In conversion of Sc_2O_3 to Sc_2S_3, the oxysulfide, ScO_2S, was found as an intermediate phase, and
339 fairly stable at 1273 K. The optimum condition to synthesize almost pure phase of Sc_2S_3 was to
340 sulfurize Sc_2O_3 at 1473 K by evaporating CS_2 liquid at 273 K. The oxygen contamination was
341 minimized to 2.22 wt%O. The reaction temperature and time directly affected the degree of
342 sulfurization, and the carbon contamination remarkably increased by increasing the evaporation
343 temperature of CS_2 because of decomposition of CS_2 to carbon and sulfur gas. The obtained Sc_2S_3
344 crystals showed the morphology of the hexagonal-shape plates. A practical method for producing a
345 large amount of Sc_2S_3 directly from the purified Sc_2O_3 has been confirmed in this work. It is, then,
346 expected to convert the oxide to pure metal Sc via Sc_2S_3, if calciothermic reduction or
347 electrochemical reduction using molten salt can be applied.

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Figure Captions

Fig.1 A schematic illustration of the experimental setup.

Fig.2 Mass change after CS_2 gas sulfurization for 7.2 ks.

Fig.3 Mass change after CS_2 gas sulfurization.

Fig.4 Apparent view of sulfurized sample at 1473 K for 7.2 ks. CS_2 liquid was hold at 273 K (a), and 313 K (b).

Fig. 5 X-ray diffraction patterns of the samples sulfurized at various temperatures for 7.2 ks.

Fig.6 X-ray diffraction patterns of the samples sulfurized at 1373 K.

Fig.7 Sulfur content of the sulfurized samples.

Fig.8 The residual oxygen content of the sulfurized samples.

Fig. 9 SEM images of (a) as-received scandium oxide and the synthesized sulfides at 1273 K (b, c), and 1473 K (d, e) for 10.8 ks.

Fig.10 Mass change of sulfurized samples for 7.2 ks at various CS_2 evaporation temperatures.

Fig. 11 Oxygen concentration of the sulfurized samples for 7.2 ks at various CS_2 evaporation temperatures.

Fig.12 Vapor pressure of CS_2 vs evaporation temperature [16].

Fig.13 Carbon content of the samples prepared by evaporation of CS_2 at various temperatures.

Fig.14 XRD pattern of sulfurized sample at 1473 K for 7.2 ks by using CS_2 gas evaporated at 313 K.

Fig.15 Potential diagram of the oxides and sulfides in the ternary Ce-O-S and Sc-O-S systems [16].