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Thermogravimetric study of the reduction and sulfurization of $Nd_2(SO_4)_3$ using carbon disulfide

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Abstract

The basic steps in the reaction of $Nd_2(SO_4)_3$ with CS_2 were studied by thermogravimetric techniques to elucidate the reaction mechanism of the formation of Nd_2S_3. The $Nd_2(SO_4)_3$ first decomposes to $Nd_2O_2SO_4$ in the range 500–650°C, depending on the heating rate. $Nd_2O_2SO_4$ is further deoxygenated to Nd_2O_2S, which forms a disulfide phase at lower temperatures (500–600°C) by reaction with CS_2. Neodymium disulfide, which exhibits a wide range of non-stoichiometry ($NdS_{1.876}$–NdS_2), decomposes into Nd_2S_3 above 600°C. At lower heating rates (1 and 5°C min^{-1}), orthorhombic Nd_2S_3 is formed in a single phase on heating to 1100°C. In contrast, non-stoichiometric cubic Nd_2S_{3-x} is formed together with orthorhombic Nd_2S_3 when the heating rate is as high as 10°C min^{-1}.

Keywords: Carbon disulphide; Neodymium disulphide; Neodymium oxysulphate; Neodymium oxysulphide; Neodymium sesquisulphide; Neodymium sulphate; TG

1. Introduction

Investigation of the solid chemistry of rare-earth (RE) sulfides is of great interest because these compounds could potentially be used as advanced compounds in the field of high technology.

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There are several methods for the preparation of rare-earth sulfides [1-8]. The method most frequently adopted consists of combination of the RE metal and sulfur, but it requires careful handling because the RE metals are highly sensitive to air oxidation and, in addition, the pure metal of the RE elements is expensive. In this situation, increased importance is attached to methods for the synthesis of RE sulfides from their compounds. Among such methods, the deoxygenation and sulfurization of RE oxides by H_2S or CS_2 are often undertaken. When the compounds are used, elevated reaction temperatures are generally needed for preparing RE sulfides which are free from oxysulfides. Carbon disulfide is known as a powerful deoxygenating reagent, but it tends to leave carbon as impurity in the sulfides, as the thermal decomposition of CS_2 is enhanced at high temperature. The sulfurizing power of H_2S, on the other hand, is weaker, requiring higher reaction temperatures than CS_2.

In a preceding paper [9], we described the preparation of the neodymium sulfides from neodymium sulfate using CS_2. Neodymium disulfide NdS_2 (or NdS_{2-x}) was found to be formed at the comparatively low temperature of 500-600°C, whereas neodymium sesquisulfide Nd_2S_3 (orthorhombic form) was formed in the temperature range 800-900°C. Several other compounds were formed as intermediates, namely $Nd_2O_2SO_4$, Nd_2O_2S, Nd_2S_{3-x} (γ-phase) and Nd_3S_4.

This study deals with the elucidation of the reaction of $Nd_2(SO_4)_3$ as well as its subsequent intermediate compounds with CS_2 in a flow of a CS_2/N_2 mixture. In order to resolve the reactions quantitatively, the reaction processes were monitored using thermogravimetric techniques.

2. Experimental

2.1. Materials

Anhydrous neodymium sulfate $Nd_2(SO_4)_3$ was obtained by heating neodymium sulfate octahydrate $Nd_2(SO_4)_3 \cdot 8H_2O$ (99.9%, purchased from Nippon Yttrium Co. Ltd.) at 450°C in a vacuum of 10 Pa for 1 h.

Neodymium oxysulfate $Nd_2O_2SO_4$ was prepared by heating neodymium sulfate octahydrate $Nd_2(SO_4)_3 \cdot 8H_2O$ at 1100°C in a stream of N_2 for 1 h. The decrease in weight (42.63 wt%) during the reaction was in good agreement with the theoretical value (42.20 wt%). The product was crystallographically identified as $Nd_2O_2SO_4$ by X-ray powder diffraction analysis.

Neodymium oxysulfide Nd_2O_2S was prepared by the reduction of $Nd_2O_2SO_4$ at 850°C in a stream of H_2 for 1 h. The observed weight loss (15.21 wt%) was in good agreement with the theoretical value of 15.36 wt%. The formation of single phase Nd_2O_2S was confirmed by X-ray diffraction analysis.

Neodymium disulfide NdS_2 was prepared by heating orthorhombic Nd_2S_3 with an excess of sulfur in a vacuum sealed quartz ampoule at 600°C for 1 day. The inner surface of the ampoule had been coated with a carbon layer in order to prevent the reaction of compounds with quartz. X-ray diffraction analysis showed that the main product was NdS_2, but a few percent of free sulfur was also observed to be present as a mixture with NdS_2.

Analytical grade CS_2 with a boiling point of 46–47°C and a maximum of 0.02% of water as impurity was obtained from Wako Pure Chemicals Co. Ltd., and used as received. Nitrogen gas of 99.99% purity was used.

2.2. *Thermogravimetric analysis*

The quartz crucible containing the weighed sample powder was suspended from a quartz spring of sensitivity 12.7 mg mm^{-1} at a position 3–5 mm above or below the center of the 30 mm uniform ($\pm 1°C$) temperature zone of a vertical tube furnace, depending on the expected weight gain or loss. The temperature was measured with a Pt/Pt + 13%Rh thermocouple in quartz shielding tube placed at the central part of the uniform temperature zone in contact with the outer wall of the quartz reaction tube. The furnace temperature was raised at a constant rate using a programmable temperature controller (Chino Co. Ltd., Model KP1130B). In this arrangement the temperature difference between the controller and sample was within 5°C. Before heating, the reaction tube was evacuated to ≈ 100 Pa and refilled with N_2 up to ambient pressure, followed by flushing the reaction tube with CS_2 in N_2 carrier gas for 30 min. The gas mixture of CS_2 and N_2 was obtained by passing N_2 gas through a bubbler containing liquid CS_2. The concentration of CS_2 in the gas mixture was calculated from the volume change of CS_2 in the bubbler. The flow rate of N_2 was measured using a Kusano FT-1/1.6-14-150 float flowmeter.

Preliminary experiments were carried out at each of the heating rates 1, 5 and 10°C min^{-1} and CS_2/N_2 gas flow rates of 50/100, 100/200 and 200/400 ml min^{-1}. According to the results, a significant change was seen in the TG curves with heating rate but almost no change with the gas flow rate. Thus, in this work, the gas flow rates were fixed at 100 and 200 ml min^{-1} for CS_2 and N_2, respectively.

2.3. *X-ray diffraction analysis*

The X-ray diffraction analysis was carried out with a Rigaku Type RAD-IC diffractometer using Ni-filtered Cu $K\alpha$ radiation (40 kV, 20 mA). The least-squares calculations of lattice parameters were carried out using the LCR2 program [10].

3. Results and discussion

The results of the TG experiments for the reaction of $Nd_2(SO_4)_3$ with CS_2 are shown in Fig. 1 as three curves for the different heating rates. The decomposition temperature of $Nd_2(SO_4)_3$ in a stream of CS_2/N_2 depends considerably on the heating rate. First, $Nd_2O_2SO_4$ is formed by the reaction

$$Nd_2(SO_4)_3 + CS_2 = Nd_2O_2SO_4 + (CO, CO_2, COS, S_2...) \quad (1)$$

In Fig. 1 the temperature of decomposition to $Nd_2O_2SO_4$ shifts to the low temperature side as the heating rate is lowered from 10°C min^{-1} to 1°C min^{-1}. At 1°C min^{-1}, the formation of $Nd_2O_2SO_4$ (identified by X-ray diffractometry) ceases

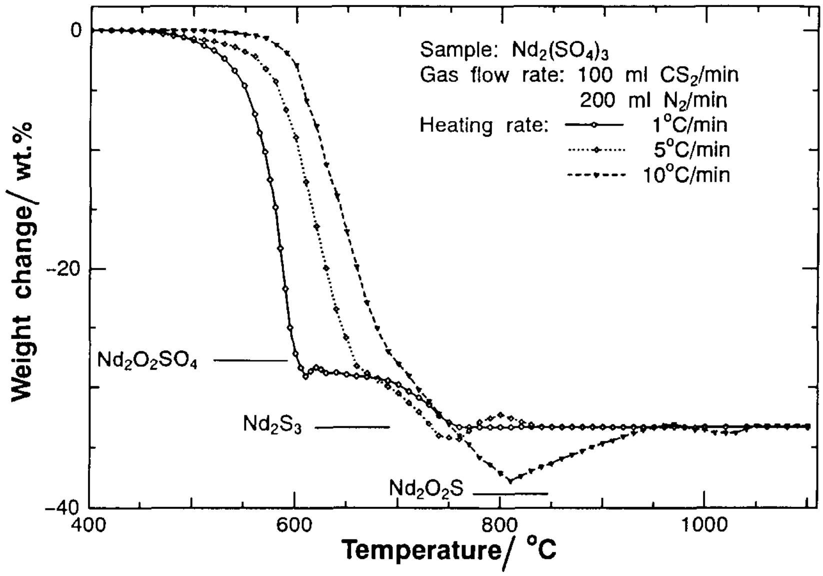

Fig. 1. TG curves of the reaction of $Nd_2(SO_4)_3$ with CS_2 at various heating rates.

at 600°C. If the small fluctuation near 600°C is disregarded, the curve continues downward as far as 750°C, above which it is horizontal, i.e. no weight change occurs above 750°C. The horizontal position corresponds to Nd_2S_3. However, the TG curves for 5 and 10°C min^{-1} are a little more complex after passing the weight change corresponding to $Nd_2O_2SO_4$, showing that the succeeding reactions overlap at such high heating rates.

The TG curve for the 10°C min^{-1} heating rate falls straightforwardly to 37.7 wt% above 800°C, which is close to the theoretical weight decrease of 38.87 wt% from $Nd_2(SO_4)_3$ to Nd_2O_2S via $Nd_2O_2SO_4$. The second step of this sequence of reactions can be written as

$$Nd_2O_2SO_4 + CS_2 = Nd_2O_2S + (CO, CO_2, COS, S_2 ...) \quad (2)$$

We will discuss this minimum in the 10°C min^{-1} TG curve later. The product after heating up to 1100°C was identified as a mixture of a cubic γ-phase (non-stoichiometric Nd_2S_{3-x}) and orthorhombic Nd_2S_3 by X-ray powder diffraction analysis. In contrast, the product was orthorhombic Nd_2S_3 in a single phase when the heating rates were 1 and 5°C min^{-1}.

Next, the reaction in CS_2/N_2 was studied using $Nd_2O_2SO_4$ as the starting material. The results are shown in Fig. 2. The reduction of $Nd_2O_2SO_4$ begins at slightly lower temperatures than those shown in Fig. 1. For heating rates of 1 and 5°C min^{-1}, after the weight had decreased by 7.65 wt% it remained unchanged on further increase of temperature. This value is in excellent agreement with the theoretical weight loss of 7.65 wt% for the formation of orthorhombic Nd_2S_3 from $Nd_2O_2SO_4$. The weight decrease of the sample heated at a rate of 10°C min^{-1} continues to 14.30 wt%, which is near the theoretical value (15.36 wt%) of reaction (2).

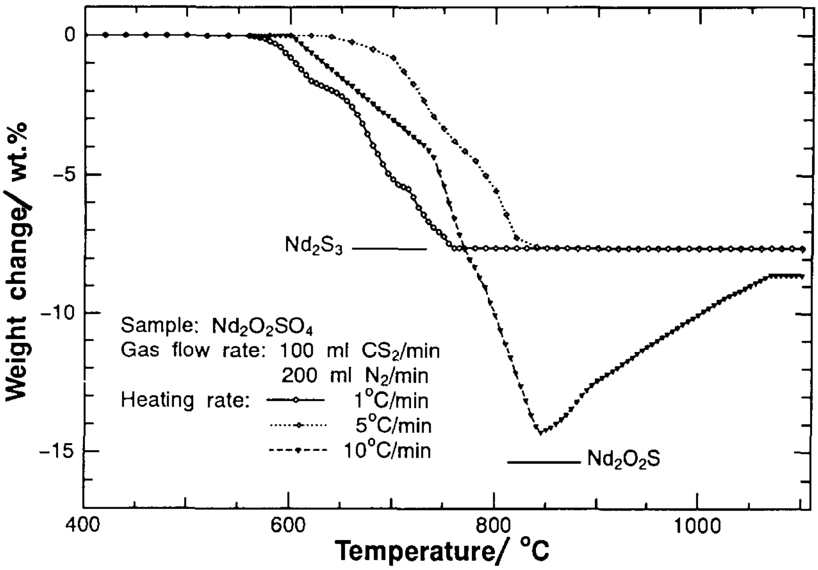

Fig. 2. TG curves of the reaction of $Nd_2O_2SO_4$ with CS_2 at various heating rates.

It is seen from the three curves in Fig. 2 that $Nd_2O_2SO_4$ changes to Nd_2S_3 via Nd_2O_2S and the rate of the reaction

$$Nd_2O_2S + CS_2 = Nd_2S_3 + (CO, CO_2, COS, S_2 ...) \qquad (3)$$

is lower than that of reaction (2). If the heating rate is low (1 or 5°C min^{-1}), the rate of formation of Nd_2O_2S is low enough to change all the Nd_2O_2S formed to Nd_2S_3. But if the rate is 10°C min^{-1}, Nd_2O_2S is rapidly formed and accumulates before it is converted to Nd_2S_3 according to reaction (3). The estimated amount of Nd_2O_2S exceeds 85 wt% at 840°C. The minimum in Fig. 1 is well resolved.

The product after heating to 1100°C was orthorhombic Nd_2S_3 in a single phase for rates of 1 and 5°C min^{-1}, whereas it was a mixture of cubic Nd_2S_{3-x} and orthorhombic Nd_2S_3 when the heating rate was 10°C min^{-1}.

Next, a thermogravimetric study of the reaction of Nd_2O_2S was carried out (Fig. 3). The shape of the TG curves in the figure is largely dependent on the heating rate. The formation of Nd_2S_3 from Nd_2O_2S is accompanied by a weight increase. But the TG curve for a heating rate of 1°C min^{-1} exhibits a maximum which is markedly larger than the weight gain of reaction (3) for the formation of Nd_2S_3. In order to examine this maximum, which should reflect the formation of an intermediate phase, another experiment was carried out in which the Nd_2O_2S sample was heated at a rate of 1°C min^{-1} in the same CS_2/N_2 gas mixture and quenched from 600°C within a few seconds. X-ray powder diffraction analysis of this specimen revealed that the phase was NdS_{2-x} together with a small amount of unreacted Nd_2O_2S. The formation of NdS_{2-x} is written as

$$Nd_2O_2S + CS_2 = 2NdS_{2-x} + (CO, CO_2, COS, S_2 ...) \qquad (4)$$

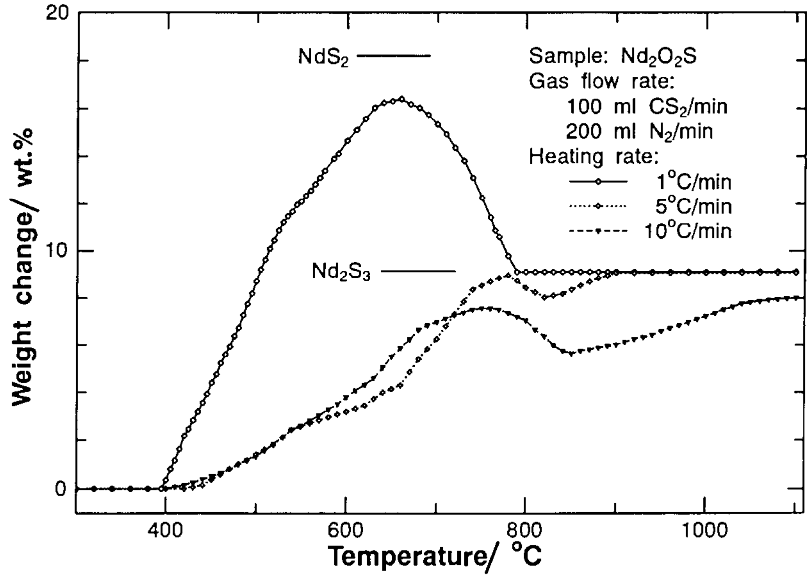

Fig. 3. TG curves of the reaction of Nd_2O_2S with CS_2 at various heating rates.

The weight gain of 16.16 wt% at 650°C on the TG curve for heating at 1°C min^{-1} in Fig. 3 is considerably smaller than the expected gain of 18.21 wt% for the formation of stoichiometric NdS_2 from Nd_2O_2S. Since the x value in NdS_{2-x} is small, the above difference is considered to be caused mainly by the continuous conversion of NdS_{2-x} into Nd_2S_3 above ≈530°C. At 5°C min^{-1}, owing to the higher heating rate, the weight gain for the formation of NdS_{2-x} shifts to the high temperature side. Moreover, the higher rate of conversion to Nd_2S_3 above 650°C depresses the peak height. The above effect becomes more evident for heating at 10°C min^{-1}, and the peak is smaller than that for 5°C min^{-1}. The larger weight change than that for the 5°C min^{-1} experiment in the 550–700°C region may result because the reaction rate of the conversion of NdS_{2-x} to Nd_2S_3 was slower than the fast temperature rise of 10°C min^{-1}.

The decomposition behavior of stoichiometric NdS_2 in a stream of CS_2/N_2 is shown in Fig. 4. The weight loss in the temperature range 200–300°C is ascribed to the removal of the free sulfur which was deposited on the NdS_2 sample when it was prepared (mentioned in the Experimental section). From the TG curve it can be seen that the amount of free sulfur was ≈2 wt%. The observed weight losses corrected for free sulfur are 7.68, 7.60 and 7.47 wt% for the heating rates of 1, 5 and 10°C min^{-1}, respectively. These values are in good agreement with the expected weight loss for the change of stoichiometric NdS_2 into Nd_2S_3, namely 7.69 wt%

$$2NdS_2 = Nd_2S_3 + 0.5S_2 \qquad (5)$$

The 1°C min^{-1} curve of Fig. 4 is horizontal around 600°C. The following reaction is assumed to take place in this temperature range

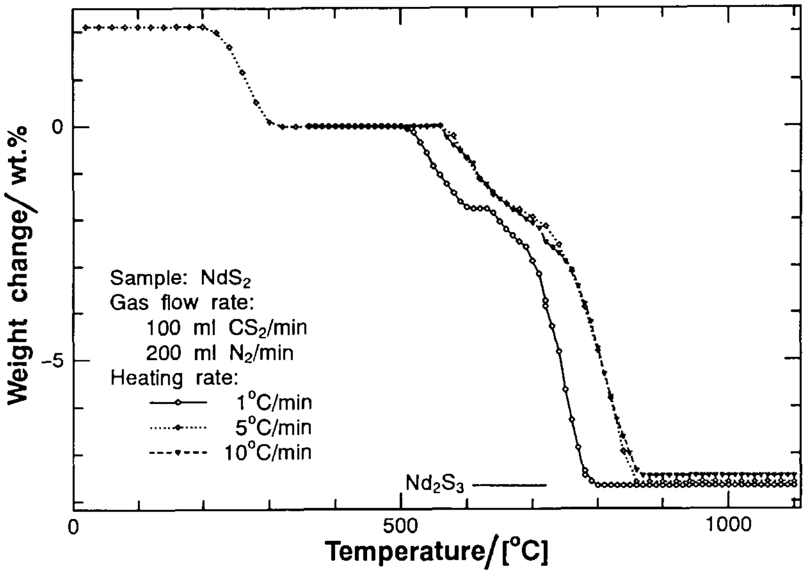

Fig. 4. TG curves of the thermal decomposition of NdS_2 in a stream of CS_2/N_2 gas mixture.

$$NdS_2 = NdS_{2-x} + x/2S_2 \qquad (6)$$

In order to verify this, X-ray diffraction analysis was carried out on the specimen which had been obtained by heating NdS_2 at a rate of 5°C min^{-1} up to 650°C followed by quenching to room temperature. In Fig. 5, the X-ray pattern of this specimen is compared with that of stoichiometric NdS_2 before heating. The patterns are quite similar and all the lines could be indexed as a tetragonal system with the lattice parameters $a = 0.3980(1)$ and $c = 0.8016(2)$ nm (Fig. 5(a)). The quenched sample is NdS_{2-x} with an x value which would give the phase limit of the NdS_{2-x} phase. The lattice parameters of this NdS_{2-x} are close to $a = 0.4012(2)$ and $c = 0.8033(3)$ for the stoichiometric NdS_2 before heating, and they are also comparable with the reported values of $a = 0.4022$ and $c = 0.8031$ nm [11]. The lattice parameter c of stoichiometric NdS_2 is nearly twice as large as a, but the departure from this ratio becomes significant for the heated sample. Thus, the (111) and (003) reflections, which compose one peak in Fig. 5(b), split into two peaks in Fig. 5(a) (inset). The X-ray diffraction data for the heated specimen contain a few very weak lines which cannot be assigned to the tetragonal system. It is possible that there is some ordering of the vacancies in this non-stoichiometric NdS_{2-x}. The x value of the quenched sample is calculated as 0.124 from the weight change in Fig. 4. This value shows that the region of non-stoichiometry extends at least up to $x = 0.124$ at 650°C, because the crystal structure is the same for NdS_2 and NdS_{2-x} if one disregards the possibility of ordering.

The preparation of neodymium disulfide was tested by heating orthorhombic Nd_2S_3 in a stream of CS_2/N_2 gas mixture. However, no weight change was observed to occur on thermogravimetry, suggesting that the sulfur pressure of CS_2 was

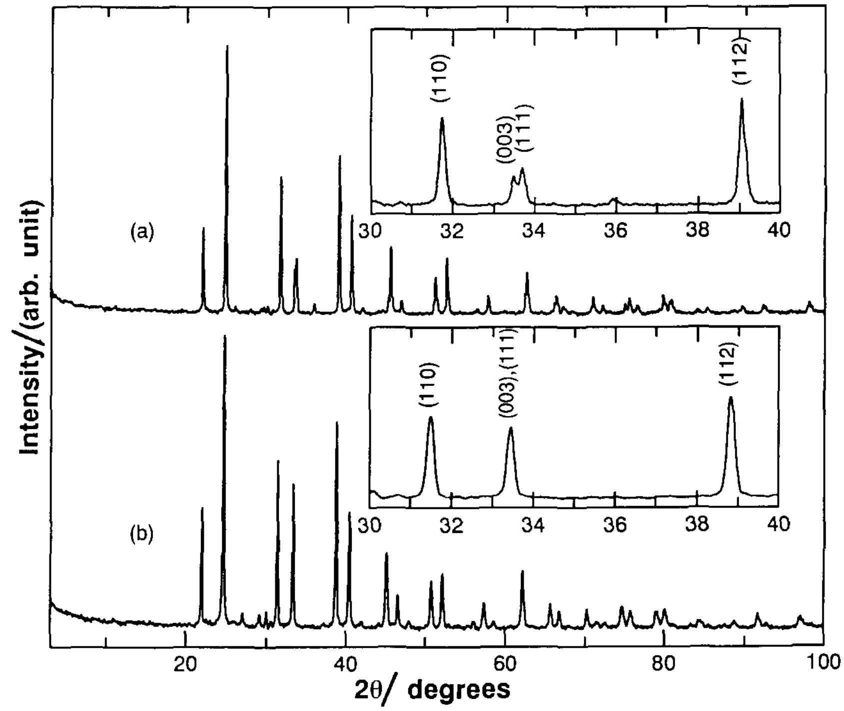

Fig. 5. X-ray diffraction patterns of neodymium disulfides: (a) after heating to 650°C and then quenching to room temperature (NdS_{2-x}); (b) before heating (NdS_2).

insufficient to convert Nd_2S_3 to the disulfide. On the other hand, when a mixture of Nd_2S_3 and $Nd_2O_2SO_4$ (50:50 by wt.) was heated in a stream of CS_2/N_2, the disulfide phase was formed at lower temperatures. The reaction gave a weight gain which would not have been observed unless Nd_2S_3 had changed to the disulfide, since the conversion of $Nd_2O_2SO_4$ to the disulfide should yield almost no weight gain. This result, together with the X-ray diffraction analysis which confirmed the formation of the disulfide phase, suggests that the active sulfur possibly liberated in reactions (2) and (3) should play an important role in the conversion of Nd_2S_3 to disulfide.

4. Conclusions

(1) The elementary reactions in the reduction and sulfurization of $Nd_2(SO_4)_3$ with CS_2 to form Nd_2S_3 were studied by means of the thermogravimetric technique.

(2) Starting from $Nd_2(SO_4)_3$, $Nd_2O_2SO_4$ is formed first. This compound changes to Nd_2O_2S, which is converted to Nd_2S_3 via NdS_2 (or NdS_{2-x}).

(3) The rate of the reaction of Nd_2O_2S and CS_2 to form Nd_2S_3 is lower than that of $Nd_2O_2SO_4$ and CS_2 to form Nd_2O_2S. Then, Nd_2O_2S is accumulated at ≈ 850°C if the heating rate is as high as 10°C min^{-1}.

(4) Neodymium disulfide (NdS_2, NdS_{2-x}) is formed at lower temperatures, around 600°C, in the reaction of Nd_2O_2S with CS_2 in the presence of sulfur vapor generated in this reaction and/or in the reaction of $Nd_2O_2SO_4$ and CS_2.

(5) Neodymium disulfide is unstable at higher temperatures and decomposes, resulting in the formation of Nd_2S_3.

(6) Orthorhombic Nd_2S_3 is formed in a single phase above 900°C when the heating rate is 1 or 5°C min^{-1}.

(7) At the high heating rate of 10°C min^{-1}, a mixture of cubic Nd_2S_{3-x} and orthorhombic Nd_2S_3 was obtained above 900°C.

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