

Low Temperature Chlorination of Nd_2O_3 by Mechanochemical Method with CCl_4

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ABSTRACT

For a chlorinating method at low temperature, the possibility of chlorination of Nd_2O_3 by a mechanochemical reaction with CCl_4 was studied using a planetary ball mill. The mechanochemical experiments were conducted by changing the pot materials, milling time, molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$, and revolution speed. As the results of obtained products by X-ray diffractometry and Raman spectroscopy, it was confirmed that the chlorination to NdOCl from Nd_2O_3 with CCl_4 was advanced at room temperature in a zirconia or tungsten pot with balls. We found that an extension of the milling time and an increase of the number of ball were effective to the chlorination to NdOCl and that tensile stress remained in the milled powder by using a planetary ball mill.

Keywords: Mechanochemical Method; Carbon Tetrachloride; Neodymium Oxide; Low Temperature Chlorination; Neodymium Oxychloride; XRD; RAMAN Spectroscopy

1. Introduction

In the non-aqueous reprocessing process for spent nuclear metallic fuels by the pyro-metallurgical method [1], a spent fuel is dissolved into the LiCl-KCl eutectic melt at 450°C - 500°C and dissolved uranium and plutonium are collected as metals by an electrolysis technique. By the contamination of oxide impurities into the process environment, these actinide ions are de-chlorinated and precipitated in the melt as oxides. In order to decrease this precipitation of actinide oxides, the atmosphere in process devices is needed to be filled with inert gas in high purity, but the contamination of oxide impurities to the atmosphere cannot prevent completely. Therefore, the study on the dissolution of actinide oxides into the melt has been conducted as the chlorination process development. In the current study [2], the uranium oxides in the LiCl-KCl eutectic melt were chlorinated to uranium chlorides by the addition of zirconium tetrachloride, ZrCl_4 , but zirconia particles were generated by this chlorination. When this adding ZrCl_4 method is assumed to apply to the practical process, it is necessary to establish the efficient technique which can separate the zirconia particles from the melt at high temperature. This development is not easy though the centrifuge is promis-

ing as this separation technique.

It is thought that the chlorinating operation of actinide oxides is appropriate at the refining treatment process of used solvent salts. This refining process is a batch operation, and the assumed procedure is as follows: After settling the melt in the electrolytic vessel, the top clear melt is transported to the other vessel, and then the rest of melt including actinide oxides is coagulated. This coagulated salt is taken out, and the actinide oxides with coexistence of solvent salt are chlorinated by the new chlorination method.

For this chlorination method, we are examining the possibility of using a mechanochemical reaction in easier operating conditions at low temperature. In the present study, the possibility of low temperature chlorination of di-neodymium tri-oxide, Nd_2O_3 , with carbon tetrachloride, CCl_4 , was studied by using a planetary ball mill. For this mechanochemical method, the sulfurization of Nd_2O_3 with carbon disulfide, CS_2 , to neodymium oxysulfide, $\text{Nd}_2\text{O}_2\text{S}$, had been confirmed at the low temperature [3]. Many studies by using a planetary ball mill were carried out, and those results were reported about the mechanical alloying [4-7], the physical effect investigation [8-10], the mechanochemical synthesis [3,11-15], etc. However, no study has been reported on the low temperature chlo-

ration of rare-earth oxides by mechanochemical treatment using CCl_4 . This method would be a potential process for the low temperature synthesis of metal oxide, especially lanthanides and actinides. In this text, the mechanochemical experiments of Nd_2O_3 with CCl_4 and the X-ray diffraction (XRD) patterns and Raman spectra of their mechanochemical products are described.

2. Experimental

2.1. Reagents

Anhydrous oxide powder of Nd_2O_3 with 99.9% in purity was purchased from Kojundo Chemical Lab. Co., Ltd., and it was treated by vacuum drying for 2 h at 200°C before the use. A reagent CCl_4 with a boiling point of 76°C - 77°C and maximum water content of 0.02% was purchased from Wako Pure Chemical Industries, Ltd. and was used without further treatment.

2.2. Apparatus

A planetary micro mill "Pulversettle 7" of Fritsch GmbH, which equipped with a pair of two pots and balls, was used for these mechanochemical experiments. Three kinds of pair pots which were made from SUS304 stainless steel, zirconia, or tungsten carbide were used. All pots have a vessel space with 40 mm in height and 40 mm in diameter, as shown in **Figure 1**. The used balls were made from the same material of pots. The densities of SUS304, zirconia, and tungsten carbide are 7.9 , 6.0 , and $15\text{ g}\cdot\text{cm}^{-3}$, respectively.

2.3. Experimental Procedure

The Nd_2O_3 powder, CCl_4 liquid and balls were put in one of pair pots, and only the balls were put in another pot. The added amounts of Nd_2O_3 and CCl_4 in the pot are adjusted to molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ with 3.47 in the

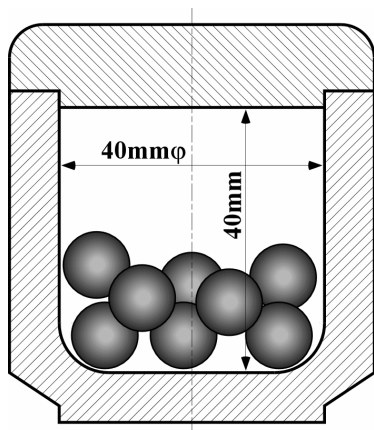


Figure 1. Schematic cross section of pot and balls in planetary ball mill.

standard condition of this study. After setting a pair pots in the planetary ball mill, the mill was operated for 0.5 - 4 h at room temperature with the revolution speed of planetary disk at 250 or 500 rpm. The transmission ratio between the revolution speed of planetary disk and the rotation speed of milling pots was 1:-2. And the rotation of the pots was set as the opposite direction to the revolution of the planetary disk, as illustrated in reference [9]. The milling operation interrupted for 15 minutes every 30 minutes milling to avoid overheating by a mechanochemical reaction. The mechanochemical experiments for Nd_2O_3 with CCl_4 were carried out in 19 conditions as shown in **Table 1**. The number of balls in a pot was selected in consideration of the standard condition described in the catalog of the planetary ball mill. However, in using a tungsten carbide pot, the number of ball was a half of the standard condition to suppress the load to the planetary ball mill.

After the milling operation, the XRD pattern of products, which were obtained by mechanochemical experiments, was measured in a continuous scan mode between 10° and 60° in 2θ by using the X-ray powder diffractometer Type RAD-IC of Rigaku Co. with a $\text{CuK}\alpha$ irradiation source at 40 kV and 20 mA monochromatized by pyrolytic graphite. Raman spectra of the products were obtained using the laser Raman spectrometer NRS-5100 of JASCO Co. and were measured in wavenumber range of $100 - 600\text{ cm}^{-1}$ for 5 s by excitation of 532 nm laser beam with 6.4 - 7.4 mW.

3. Results and Discussions

3.1. Products Obtained from Nd_2O_3 with CCl_4 by Using a Planetary Ball Mill

Figure 2 shows the XRD patterns of products obtained by a milling of Nd_2O_3 reagent powder with CCl_4 for 1 h at room temperature. The XRD pattern of Nd_2O_3 powder before a milling showed sharp peaks as shown in **Figure 2(a)**. The positions of their peaks at 26.8° , 29.8° , 30.8° , 40.5° , 47.4° , 53.5° , 56.9° , and 57.6° were corresponding to the International Centre for Diffraction Data JCPDS41-1089 of Nd_2O_3 , and the other small peaks at 15.9° , 27.8° , 28.7° , and 49.7° were identified as neodymium tri-hydroxide, $\text{Nd}(\text{OH})_3$, of JCPDS83-2035. The reason that $\text{Nd}(\text{OH})_3$ was identified in the Nd_2O_3 reagent, was thought that Nd_2O_3 was prepared by a wet method. Bernal *et al.* had observed that the XRD pattern of $\text{Nd}(\text{OH})_3$ in the Nd_2O_3 powder increased with an increase of the exposure time in air [16]. When the Raman spectrum of the Nd_2O_3 reagent was measured as shown in **Figure 3(a)**, the vibration bands by the Nd_2O_3 trigonal symmetry crystal observed at 106 , 428 , and 436 cm^{-1} [17]. Moreover, the color of Nd_2O_3 is light blue and $\text{Nd}(\text{OH})_3$ shows a light violet. The Nd_2O_3 reagent showed a light blue and

Table 1. Experiment condition by mechanochemical reaction.

run No.	Nd_2O_3 (g)	CCl_4 (ml)	Molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$	Material of pot & ball	Number of ball	Revolution (rpm)	Milling time (h)
1	0.2	0.2	3.47	SUS304	7	500	0.5×2
2	0.2	0.2	3.47	zirconia	16	500	0.5×2
3	0.4	0.4	3.47	tungsten carbide	8	500	0.5×2
4	0.4	0.4	3.47	zirconia	16	500	0.5×1
5	0.4	0.4	3.47	zirconia	16	500	0.5×2
6	0.4	0.4	3.47	zirconia	16	500	0.5×4
7	0.4	0.4	3.47	zirconia	16	500	0.5×8
8	0.4	0.4	3.47	zirconia	8	500	0.5×4
9	0.4	0.4	3.47	zirconia	8	500	0.5×8
10	0.4	0.4	3.47	zirconia	12	500	0.5×4
11	0.4	0.4	3.47	zirconia	24	500	0.5×4
12	0.4	0.2	1.73	zirconia	16	500	0.5×4
13	0.4	0.8	6.93	zirconia	16	500	0.5×4
14	0.4	0.8	6.93	zirconia	16	500	0.5×8
15	0.4	0.4	3.47	zirconia	16	250	0.5×2
16	0.4	0.4	3.47	zirconia	16	250	0.5×4
17	0.4	0.4	3.47	tungsten carbide	8	500	0.5×4
18	0.4	0.4	3.47	tungsten carbide	8	500	0.5×8
19	0.4	0.4	3.47	tungsten carbide	8	250	0.5×4

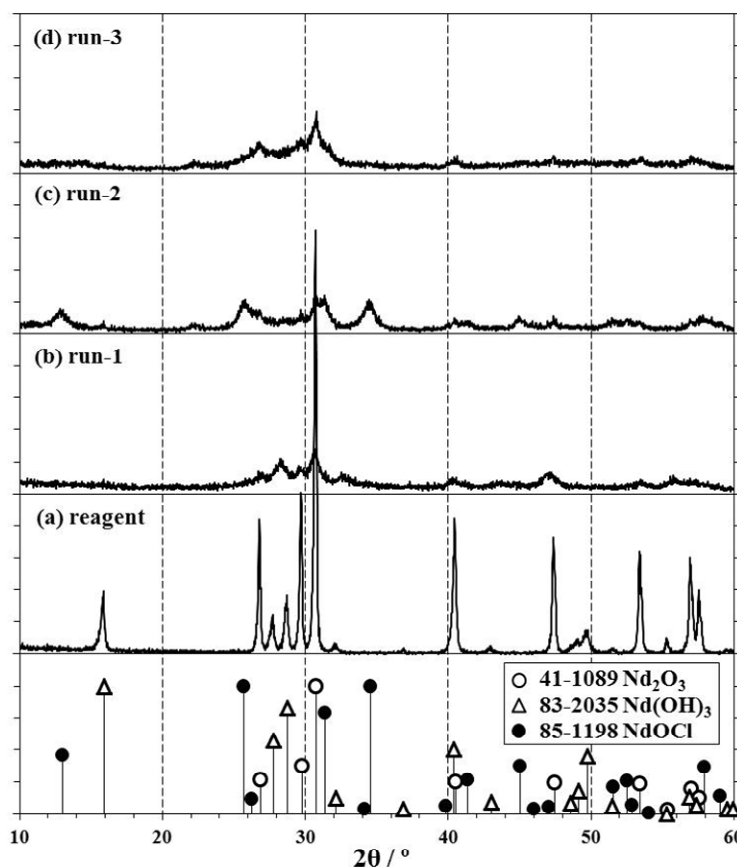


Figure 2. XRD patterns of (a) Nd_2O_3 reagent and (b)–(d) products by milling for 1 h at 500 rpm. The product of (b) run-1 was operated in SUS304 pot with $15 \text{ mm}\phi \times 7$ balls, that of (c) run-2 was in zirconia pot with $10 \text{ mm}\phi \times 16$ balls, and that of (d) run-3 was in tungsten carbide pot with $10 \text{ mm}\phi \times 8$ balls. 1 span of Y-axis is 100 cps.

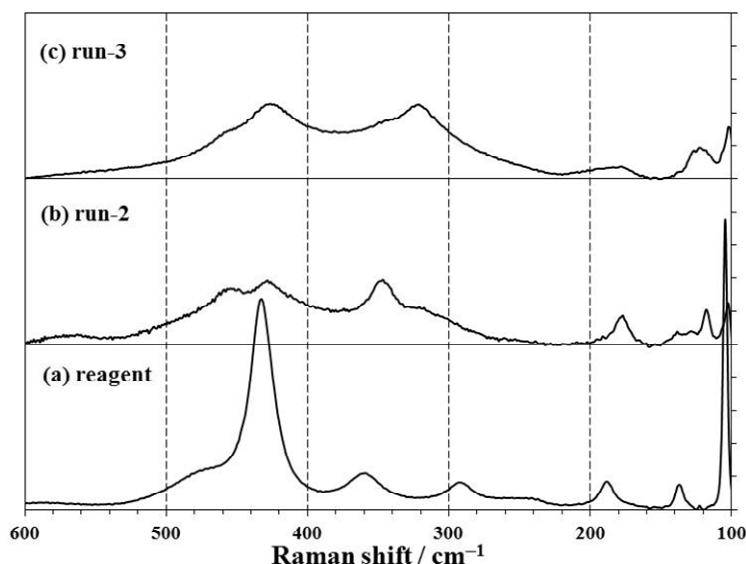


Figure 3. Raman spectra of (a) Nd_2O_3 reagent, (b) and (c) products by milling for 1 h at 500 rpm. The product of (b) run-2 was in zirconia pot with $10\text{ mm}\phi \times 16$ balls and that of (c) run-3 was in tungsten carbide pot with $10\text{ mm}\phi \times 8$ balls. 1 span of Y-axis is 25 counts.

$\text{Nd}(\text{OH})_3$ was thought not to be contained so much in the Nd_2O_3 reagent.

As for the product by a milling at 500 rpm for 1 h in a SUS304 pot with $15\text{ mm}\phi \times 7$ balls of run-1, the product discolored to blackish from light blue of Nd_2O_3 . The XRD pattern of this product was extremely gradual as shown in **Figure 2(b)**, and new broad peaks appeared at 28.2° , 29.5° , and 32.5° . These peaks were different from several peaks of the JCPDS41-1089 of Nd_2O_3 , the JCPDS83-2035 of $\text{Nd}(\text{OH})_3$, and the JCPDS85-1198 of neodymium oxy-chloride, NdOCl , and were thought to be depended on the compound generated by a reaction of SUS304 compositions with Nd_2O_3 or CCl_4 . This result indicated that Nd_2O_3 was not chlorinated by a milling with CCl_4 in a SUS304 pot and balls.

In the XRD pattern of the product obtained by a milling at 500 rpm for 1 h in a zirconia pot with $10\text{ mm}\phi \times 16$ balls of run-2, new broad peaks appeared as shown in **Figure 2(c)**. These peaks were corresponding to peaks of the JCPDS85-1198 of NdOCl at 13.0° , 25.7° , 31.4° , and 34.5° . The color of this product was light blue near the mauve color of neodymium tri-chloride, NdCl_3 , and the color of NdOCl single crystals was pale purple [18]. Thus, it was thought that the product obtained by a milling of Nd_2O_3 with CCl_4 in a zirconia pot and balls was NdOCl . However, the peak at 30.8° of Nd_2O_3 was observed in this XRD pattern, and the chlorination from Nd_2O_3 with CCl_4 was thought not to complete by a milling for 1 h. Therefore, it was confirmed the possibility that NdOCl was synthesized from Nd_2O_3 with CCl_4 by using a planetary ball mill in a zirconia pot and balls, though the Nd_2O_3 remained in the product.

Moreover, the XRD pattern of the product obtained by

a milling at 500 rpm in a tungsten carbide pot with $10\text{ mm}\phi \times 8$ balls of run-3 was not observed new peaks as shown in **Figure 2(d)**, though the peaks of Nd_2O_3 became extremely gradual. And this product did not change color and kept a light blue color of Nd_2O_3 . From the above results, it was thought that the milling time for 1 h was not enough to chlorinate from Nd_2O_3 with CCl_4 to NdOCl in a tungsten carbide pot and balls.

The XRD patterns and Raman spectra of products by mechanochemical experiments of run-4 to run-19 are shown in **Figures 4** and **5**, respectively.

3.2. Possibility of Chlorination to NdOCl by Milling in Zirconia or Tungsten Carbide Pot

As described in the above section, the milling for 1 h in a tungsten carbide pot with $10\text{ mm}\phi \times 8$ balls was not enough to chlorinate to NdOCl . According to the computer simulation in a planetary ball milling, the specific impact energy in a milling is proportional to the mass of balls [8,9]. If the NdOCl amount in a product obtained by a milling was proportional to the impact energy, this NdOCl amount by a milling in a tungsten carbide pot should be more than that in a zirconia pot because the density of tungsten carbide is 2.5 times of zirconia. On the same milling conditions, it was presumed that the NdOCl amount in a product obtained in a tungsten carbide pot increased more than that in a zirconia pot.

In order to confirm the possibility of chlorination from Nd_2O_3 with CCl_4 in a tungsten carbide pot and to compare a product obtained in a zirconia pot with that in a tungsten carbide pot, the mechanochemical experiments were conducted in the same condition by a milling at 500

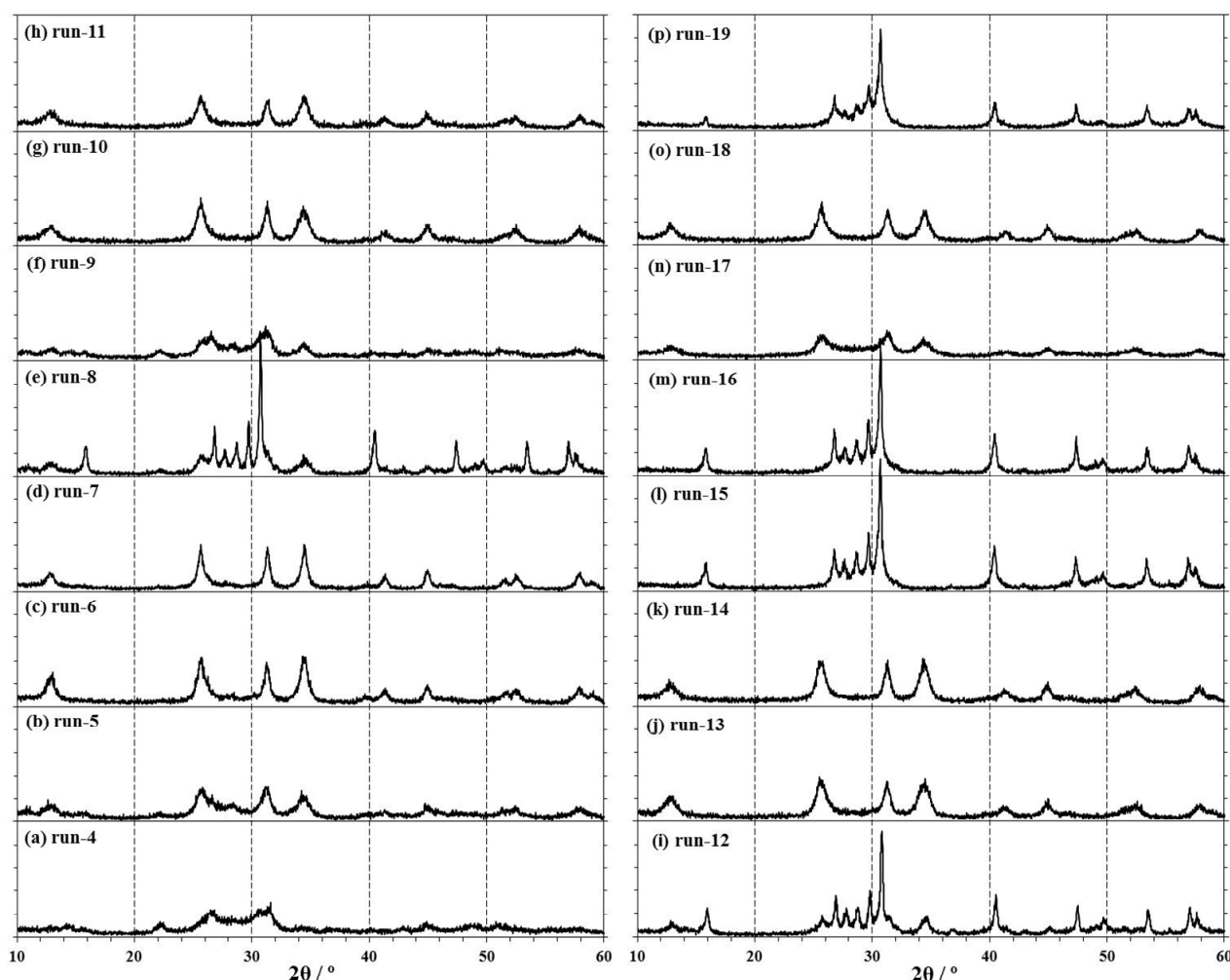


Figure 4. XRD patterns of products obtained by mechanochemical experiments of run-4 to run-19. The experimental conditions are described in Table 1. 1 span of Y-axis is 100 cps.

rpm for 4 h in a zirconia (run-9) or tungsten carbide (run-18) pot with each $10 \text{ mm}\phi \times 8$ balls. The XRD patterns of these products are shown in **Figures 4(f)** and **(o)**. It was observed that the XRD patterns of both products in a zirconia and tungsten carbide pot were contained the clear peaks of NdOCl at 13.0° , 25.7° , 31.4° , and 34.5° , suggesting that NdOCl was formed from Nd_2O_3 with CCl_4 in a zirconia or tungsten carbide pot with 8 balls. Moreover, when the Raman spectra of those products as shown the in **Figures 5(f)** and **(o)** were measured, these products were observed the Raman shifts at 118, 176, 344, and 453 cm^{-1} . The Raman shifts of tetragonal NdOCl are 118, 183, 352, and 465 cm^{-1} and these products were considered to be NdOCl [19]. As a reason to which measured peak positions became lower than reference values [19], since the Raman peak positions of RuO_2 shifted to lower wavenumber by residual stress [20-22], it was presumed that stress remained in the products even after a milling operation.

We found that NdOCl was synthesized in a tungsten

carbide or zirconia pot with balls, and that the generation of NdOCl by a milling in a tungsten carbide pot was easier than that in a zirconia pot. Therefore the higher impact energy is needed to chlorinate to NdOCl, and the NdOCl amount in the product increases with an increase of the impact energy. In other words, the use of pot and balls made of a heavy density material is effective to obtain higher impact energy for the chlorination to NdOCl by a planetary ball milling. Because the mechanical load to the milling equipment increases with an increase of the impact energy, it is necessary to select a milling condition below the limitation of the equipment. In the present study by using a tungsten carbide pot and balls, the number of ball was performed by 8 balls to prevent the failure of this planetary ball mill.

3.3. Influence on Chlorination to NdOCl by Milling Time

To confirm the effect of the chlorination to NdOCl by

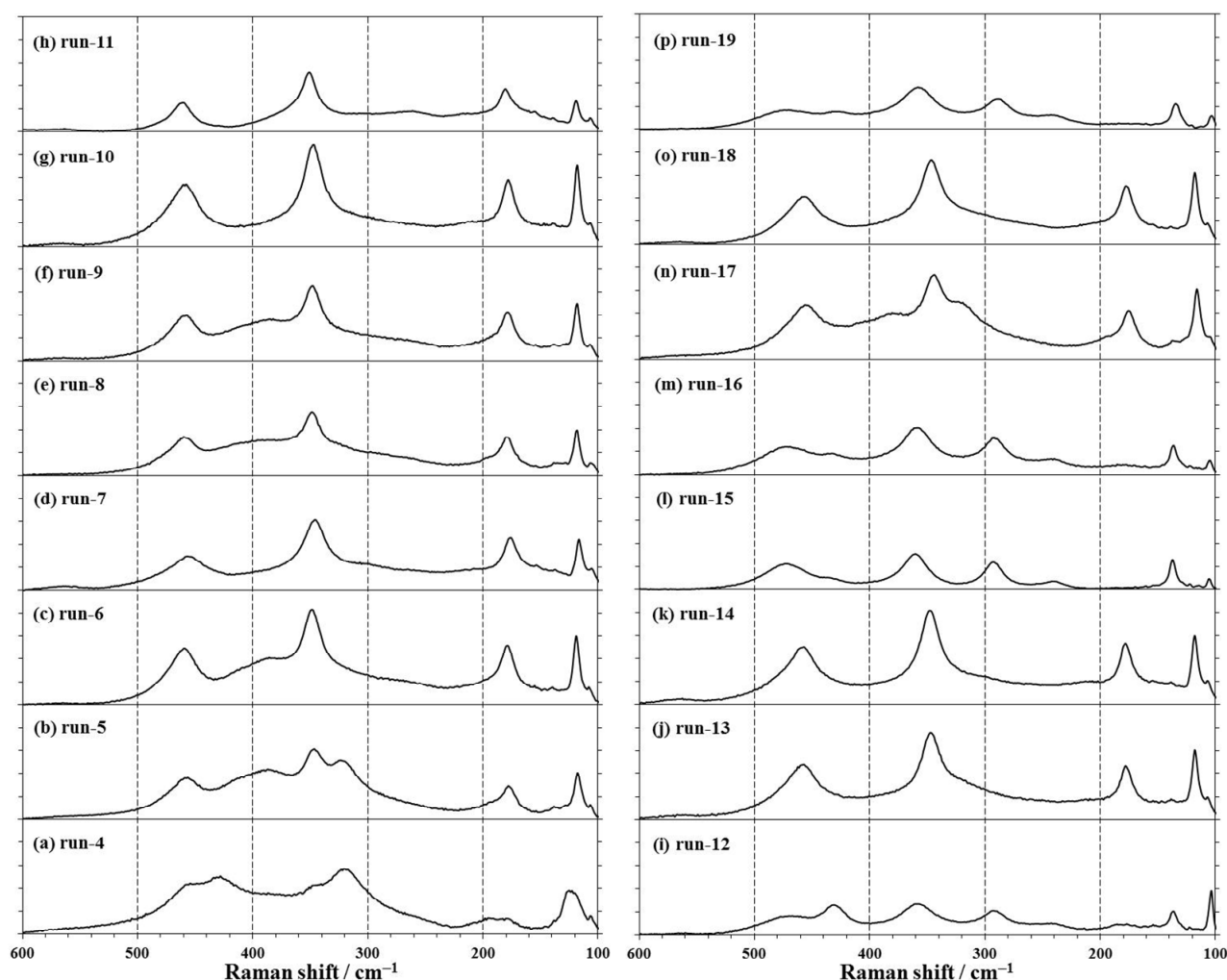


Figure 5. Raman spectra of products obtained by mechanochemical experiments of run-4 to run-19. The experimental conditions are described in Table 1. 1 span of Y-axis is 25 counts.

extending the milling time, the milling operation was carried out for the different milling time of 0.5, 1, 2, and 4 h in a zirconia pot with $10 \text{ mm}\phi \times 16$ balls or a tungsten carbide pot with $10 \text{ mm}\phi \times 8$ balls. As shown in **Figures 4 (a)–(d)**, it can be confirmed that NdOCl peaks of XRD patterns of products obtained in a zirconia pot became sharper with an extension of the milling time and that Nd_2O_3 peaks in the XRD patterns disappeared simultaneously. The pattern of run-4 by a milling for 0.5 h as shown in **Figure 4(a)** was not observed any clear NdOCl peak, and that of run-5 by a milling for 1 h as shown in **Figure 4(b)** was confirmed main NdOCl peaks at 13.0° , 25.7° , 31.4° , and 34.5° . When the milling time was extended to 2 h of run-6, these NdOCl peaks were observed more clearly as shown in **Figure 4(c)**. However, the peaks of run-6 did not have a difference with those of 4 h milling of run-7 as shown in **Figure 4(d)**. As for the Raman spectra shown in **Figures 5(a)–(d)**, the NdOCl peaks were observed in all the products. And those peaks

in products increased with an expansion of the milling time until 2 h, but those peaks of the product by a milling time for 4 h of run-7 decreased as shown in **Figure 5(d)**. Since the synthesized NdOCl crystals were ground by milling in planetary ball mill, it is presumed that the NdOCl peaks of Raman spectra decreased with excessive milling time. These results of XRD patterns and Raman spectra were thought to indicate that the chlorination to NdOCl was almost completed until 2 h of the milling time in a zirconia pot with $10 \text{ mm}\phi \times 16$ balls.

In another case of using a tungsten carbide pot with $10 \text{ mm}\phi \times 8$ balls, NdOCl peaks of XRD patterns of products increased with extending the milling time of 1, 2, and 4 h as shown in **Figures 2(d)**, **4(n)** and **(o)**. Also NdOCl peaks of Raman spectra of the products became sharper with an expansion of milling time as shown in **Figures 3(c)**, **5(n)** and **(o)**. These results indicated that the chlorination to NdOCl from Nd_2O_3 with CCl_4 was not completed by a milling for 2 h. In other words, it can be

said that the milling time more than 4 h is needed for the chlorination to NdOCl when a tungsten carbide pot with 10 mm ϕ \times 8 balls is used.

As these results, it was confirmed that an extension of the milling time was effective in completing the chlorination from Nd₂O₃ to NdOCl by using a planetary ball mill.

3.4. Influence on Chlorination to NdOCl by Molar Ratio of CCl₄/Nd₂O₃

As described in above sections, it was found that NdOCl was produced from Nd₂O₃ with CCl₄ by using a planetary ball mill. In the present study, the standard molar ratio of CCl₄/Nd₂O₃ was selected to be 3.47. If NdOCl could generate by the Reaction (1), the molar ratio would be enough with CCl₄/Nd₂O₃ = 0.5. Since CCl₄ has the low boiling point, the initial amount of CCl₄ needs to take carrying out an evaporation loss of CCl₄ from a pot during a milling operation. However, when CCl₄ is added superfluously into a pot, it is necessary to remove CCl₄ which remained in the product.

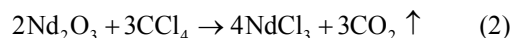


To confirm to the suitable molar ratio of CCl₄/Nd₂O₃, the mechanochemical experiments were carried out by a milling at 500 rpm for 2 and 4 h in a zirconia pot with 10 mm ϕ \times 16 balls in the condition of CCl₄/Nd₂O₃ = 1.73, 3.47, and 6.93. At the molar ratio of CCl₄/Nd₂O₃ = 1.73 by a milling for 2 h of run-12, there were large peaks of the Nd₂O₃ reagent and small NdOCl peaks in the XRD pattern of the product as shown in **Figure 4(i)**. Also in the Raman spectra of this product of run-12 as shown in **Figure 5(i)**, NdOCl peaks were small and Nd₂O₃ peaks were mainly observed. On the other hand, NdOCl peaks were observed in the XRD patterns and Raman spectra of the products by a milling for 2 h in the molar ratio of CCl₄/Nd₂O₃ = 3.47 of run-6 and 6.93 of run-13 as shown in **Figures 4(c), (j), 5(c) and (j)**, respectively. The difference in the XRD patterns of products by a milling in the molar ratio of CCl₄/Nd₂O₃ = 3.47 of run-6 and 6.93 of run-13 was not observed as shown in **Figures 4(c) and (j)**, but the NdOCl peaks of the Raman spectrum in the molar ratio of CCl₄/Nd₂O₃ = 3.47 of run-6 became slightly higher than those in CCl₄/Nd₂O₃ = 6.93 of run-13 as shown in **Figures 5(c) and (j)**. Since the balls were thought to slide on the pot inner face and the NdOCl synthesis did not advance when there was too much CCl₄ liquid volume in a case of run-13, it is presumed that the NdOCl peaks of the Raman spectra did not increase with increasing of the molar ratio of CCl₄/Nd₂O₃.

When the milling was operated for 4 h, the XRD pattern in the molar ratio of CCl₄/Nd₂O₃ = 3.47 of run-7 is similar to that of CCl₄/Nd₂O₃ = 6.93 of run-14 as shown in **Figures 4(d) and (k)**. However, as for the Raman

spectra as shown in **Figures 5(d) and (k)**, the NdOCl peaks in the molar ratio of CCl₄/Nd₂O₃ = 6.93 was slightly higher than those in CCl₄/Nd₂O₃ = 3.47. At an initial state of milling operation in a case of too much CCl₄ liquid volume of run-14, the balls were thought to slide on the inner wall of the pot as well as run-13, but the NdOCl synthesis could advance with decreasing CCl₄ liquid volume by the vaporization. In the molar ratio of CCl₄/Nd₂O₃ = 3.47 of run-7, the NdOCl synthesis advanced, but it is presumed that the NdOCl peaks of Raman spectra decreased because the synthesized NdOCl crystals at the Reaction (1) were ground by the continued milling operation in planetary ball mill.

Therefore, it can be said that the molar ratio of CCl₄/Nd₂O₃ = 3.47 is enough to synthesize NdOCl from 0.4 g of Nd₂O₃ with CCl₄ by a milling at 500 rpm for 2 or 4 h in a zirconia pot and balls. Since the initial amount of CCl₄ against Nd₂O₃ fully existed in condition of the molar ratio of CCl₄/Nd₂O₃ = 6.93, the chlorination to NdCl₃ by the reaction (2) had been expected. But the generation of NdCl₃ was not confirmed in these experiments.



3.5. Influence on Chlorination to NdOCl by Number of Ball

From results described in above sections, it was clear that the chlorination to NdOCl requires the sufficient impact energy and the number of collision of a ball against other balls or the pot wall. An extension of the milling time described in the above section means an increase of the number of collision, and an increase of the number of ball was also expectable as a method of increasing the number of collision.

To confirm the influence on the chlorination to NdOCl by the number of ball, the mechanochemical experiments were carried out by a milling at 500 rpm for 2 h in a zirconia pot with 10 mm ϕ \times 8, 12, 16, and 24 balls. In a case of 8 balls, the Nd₂O₃ peaks of a XRD pattern of run-8 were observed as shown in **Figure 4(e)**. When the number of ball was more than 12 or more of run-10, -6, and -11, the Nd₂O₃ peaks disappeared and the NdOCl peaks were observed as shown in **Figures 4(c), (g) and (h)**. In the other words, it was confirmed that the number of ball was required 12 or more for the chlorination to NdOCl from Nd₂O₃ with CCl₄ by a milling at 500 rpm in a zirconia pot. Comparing these patterns in **Figures 4(c), (e), (g) and (h)**, the pattern by a milling with 16 balls of run-6 was the sharpest. In the case of putting 24 balls in a pot, it was presumed that the motion of balls in a pot was restrained and the number of collision decreased in this milling condition. Consequently, it is considered that the XRD pattern with 24 balls was not clearer than that with 16 balls.

As for the Raman spectra, the NdOCl peaks were observed in all the products. Comparing these spectra as shown in **Figures 5(c), (e), (g) and (h)**, the NdOCl peaks in a product of run-10 in a case of putting 12 balls were higher than those of run-8 in a case of 8 balls, and were similar to those of run-6 in a case of 16 balls. But those peaks in the product of run-11 in a case of 24 balls as shown in **Figure 5(h)** were lower than those in 12 or 16 balls of run-6. The reason to which the NdOCl peaks decreased with increasing to 24 balls was presumed that the motion of balls in a pot was restrained and the number of collision decreased in this milling condition.

Therefore, it was found that the number of collision increased with an increase of the number of ball on the conditions which the number of ball was 16 or less, and it is thought that 16 balls are suitable in this milling condition.

3.6. Chlorination Effect by Revolution Speed

The revolution speed of planetary disk is one of important parameters of the impact energy in operating a planetary ball mill [8,9]. The impact energy increases with an increase of the revolution speed, but the failure risk of the mill increases with an increase of the impact energy. To decrease this risk, additional experiments of run-15, -16 in a zirconia pot and run-19 in a tungsten carbide pot were carried out in the condition of the revolution speed at 250 rpm. The conditions of run-15, -16, and -19 except the revolution speed were similar to those of run-5, -6, and -17, respectively.

As results shown in **Figures 4(l), (m) and (p)**, all XRD patterns of products of run-15, -16, and -19 by milling at 250 rpm were similar to that of a source material of Nd_2O_3 , and any peak of NdOCl were not observed. As for the Raman spectra in **Figure 5(l), (m) and (p)**, the NdOCl peaks of products of run-15, -16, and -19 by milling at 250 rpm were smaller than those of products of run-5, -6, and -17 at 500 rpm as shown in **Figures 5(b), (c) and (n)**. And the color of these products was not changed from a light blue of Nd_2O_3 . According to the simulation in a planetary ball milling [8], the impact energy was proportional to the square of the collision speed of balls, and the relation between this collision speed and the revolution speed had a correlation near proportion accurately though was not proportion. Therefore, it was confirmed that the chlorination to NdOCl from Nd_2O_3 with CCl_4 was not able to perform by a milling in the revolution speed at 250 rpm, which the impact energy was one-quarter of that at 500 rpm.

3.7. Thermodynamic Consideration for Chlorination of Nd_2O_3 with CCl_4

To understand the chlorination to NdCl_3 from Nd_2O_3 with CCl_4 described in above sections, their thermody-

namic reaction was examined using a thermodynamic data base of the MALT [23].

Figure 6 shows the temperature dependence of the Gibbs free energy changes, ΔG° , of the formation of NdOCl and NdCl_3 from Nd_2O_3 with CCl_4 , and NdCl_3 from NdOCl with CCl_4 . The ΔG° of formation of both NdOCl and NdCl_3 from Nd_2O_3 are negative values in the temperature range from 100°C to 900°C. The ΔG° of NdOCl is more negative than that of NdCl_3 . In other words, the formation of NdOCl should be caused easily thermodynamically than that of NdCl_3 . However, when the Nd_2O_3 powder reagent immersed in CCl_4 liquid for 24 h at room temperature and the XRD pattern of the reagent after the immersion was measured, the XRD pattern was similar to the initial Nd_2O_3 reagent. Therefore, the generation to NdOCl from Nd_2O_3 with CCl_4 is thought to be very slow at room temperature.

From the results estimated by the MALT in calculating condition with total pressure of 1 atm, the potential diagram of the $\text{Nd-O}_2\text{-Cl}_2$ system at 25°C, 100°C, and 200°C was drawn in **Figure 7**. According to the mechanical alloying studies [4,5], the temperature of a ball surface at a collision was estimated to be at 200°C - 500°C. And the decomposition pressures of a source reagent of CCl_4 to Cl_2 and a by-product material of CO_2 to O_2 at 25°C, 100°C, and 200°C are showed as lines in **Figure 7**. Nd is chlorinated to NdCl_3 with increasing a partial pressure of Cl_2 , and oxidized to Nd_2O_3 with increasing a partial pressure of O_2 . But in our mechanochemical experiments, NdOCl was obtained in an atmosphere condition of

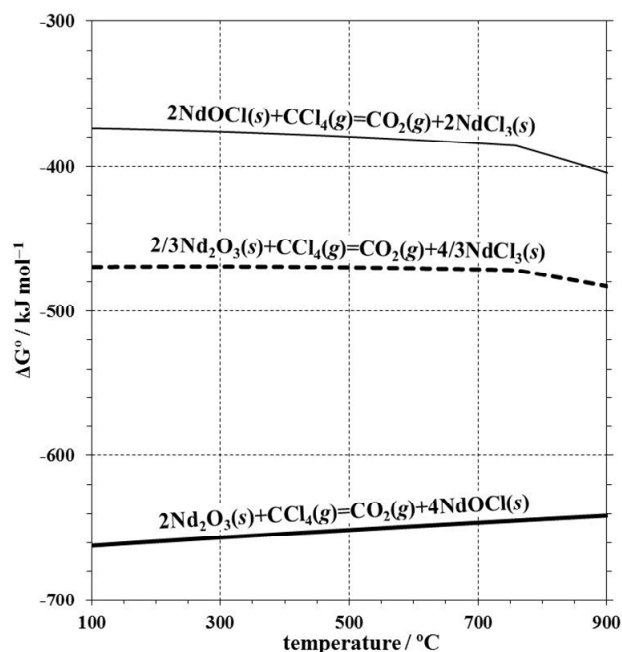


Figure 6. Temperature dependence of the Gibbs free energy changes, ΔG° , from Nd_2O_3 with CCl_4 to NdOCl or NdCl_3 , and from NdOCl with CCl_4 to NdCl_3 .

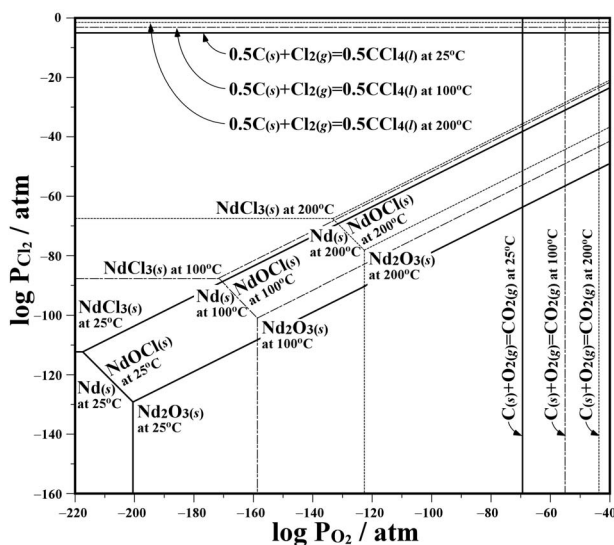


Figure 7. Potential diagram of the Nd-O₂-Cl₂ system at different temperatures. The data at 25°C, 100°C, and 200°C are given as solid, chain and dotted lines, respectively.

coexisting with Cl₂ and O₂. This NdOCl is presumed to be an intermediate product to NdCl₃. As a reason why these products were NdOCl, the generation to NdCl₃ from NdOCl with CCl₄ is thought to be very slow in our experimental conditions as well as the generation to NdOCl from Nd₂O₃ with CCl₄ at room temperature. On the other hand, if the generation to NdCl₃ from NdOCl would not be slow, it is presumed that the partial pressure of Cl₂ in a pot did not reach to the processing condition of NdCl₃ from the potential diagram of the Nd-O₂-Cl₂ system as shown **Figure 7**. That is, in order to enable generation of NdCl₃ from Nd₂O₃ by using a planetary ball mill, it is necessary to perform either of an increase of the partial pressure of Cl₂ in the pot or a large extension of the milling time.

3.8. Structural Change of Nd₂O₃ and NdOCl Powder by Milling Treatment

As described in above sections, NdCl₃ was not synthesized from Nd₂O₃ with CCl₄, but NdOCl could be obtained easily at room temperature by using a planetary ball mill. The chlorination from Nd₂O₃ to NdOCl was very slow when Nd₂O₃ was immersed in CCl₄ liquid, and it was confirmed that this chlorination progressed with expansion of the milling time by using a planetary ball mill. In the early stage of a milling operation, it was thought that the pulverization of Nd₂O₃ reagent progressed before chlorination of from Nd₂O₃ to NdOCl.

To confirm the structural change of Nd₂O₃ and NdOCl powders by using a planetary ball mill, the raw Nd₂O₃ reagent, dried Nd₂O₃ and prepared NdOCl powders were milled in each a zirconia pot with 16 balls for 0.5 h with revolution speed at 500 rpm. The dry treatment of Nd₂O₃

powder was heated the raw Nd₂O₃ reagent in air at 700°C for 1 h, and the preparation of NdOCl powder was raw Nd₂O₃ and NdCl₃ reagents mixture and heated in air at 300°C for 5 h. **Figures 8** and **9** show the XRD patterns and Raman spectra of the powders before and after a milling, respectively. Here, the XRD patterns were measured in an irradiation condition at 40 kV and 40 mA, and the Raman spectroscopy were performed on the same conditions described in above sections.

The XRD patterns of the milled Nd₂O₃ and NdOCl powders as shown in **Figures 8(b)**, **(c)** and **(e)** were smaller and broader than those of the powders before the milling treatment, respectively. The large peaks of Nd(OH)₃ were existed in the XRD pattern of a raw Nd₂O₃ reagent as shown in **Figure 2(a)**, and the pattern of Nd₂O₃ powder immediately after the dry treatment hardly observed Nd(OH)₃ peaks as shown in **Figure 8(a)**. From the weight loss of raw Nd₂O₃ reagent by the dry treatment, the amount of Nd(OH)₃ contained in the raw reagent was estimated as 48.6 wt%. Comparing the XRD patterns of milled Nd₂O₃ powders as shown in **Figures 8(b)** and **(c)**, the peaks of NdOOH at 16° and 22° were observed in the milled raw Nd₂O₃ reagent containing Nd(OH)₃. As for the generation of NdOOH, it has been

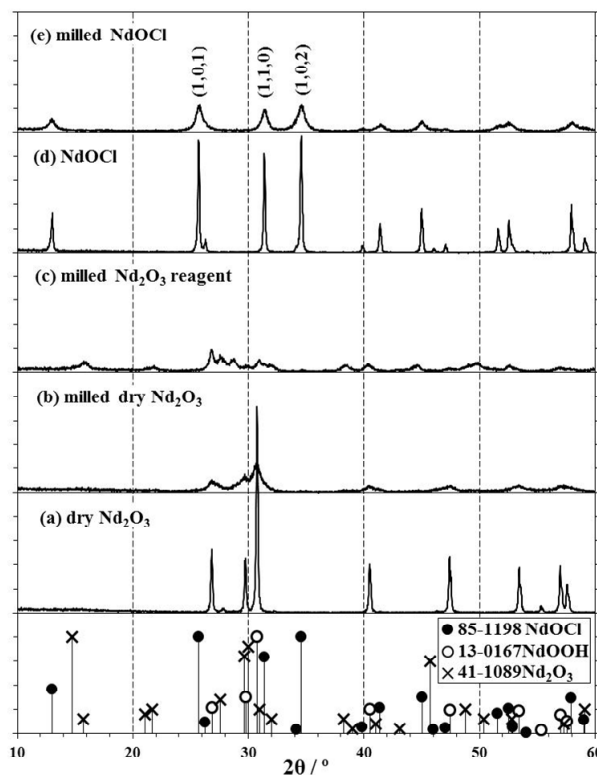


Figure 8. XRD patterns of (a) dry Nd₂O₃, (b) milled dry Nd₂O₃, (c) milled Nd₂O₃ reagent without dry treatment, (d) NdOCl, and (e) milled NdOCl. The milling condition of (b), (c), and (e) is in zirconia pot with 10 mmφ × 16 balls for 2 h at 500 rpm. 1 span of Y-axis is 100 cps.

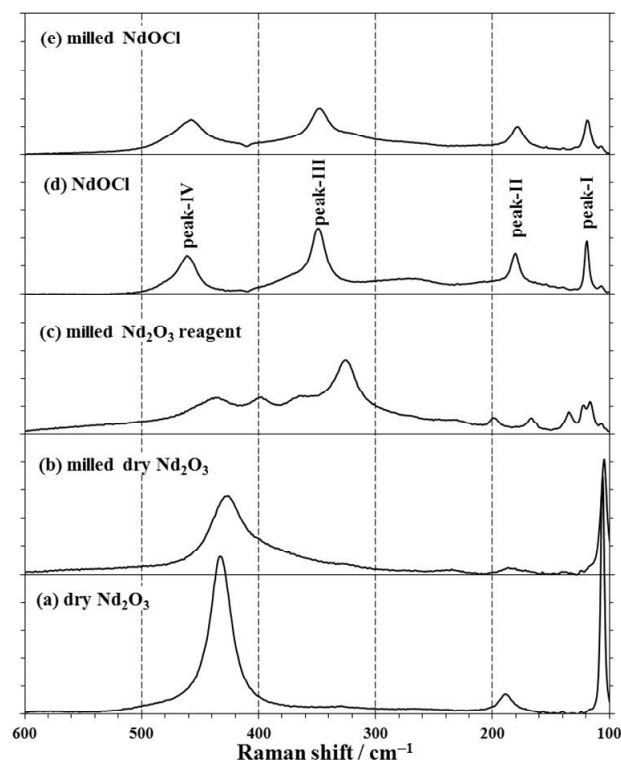


Figure 9. Raman spectra of (a) dry Nd_2O_3 , (b) milled dry Nd_2O_3 , (c) milled Nd_2O_3 reagent without dry treatment, (d) NdOCl , and (e) milled NdOCl . The milling condition of (b), (c), and (e) is in zirconia pot with 10 mm $\phi \times 16$ balls for 2 h at 500 rpm. 1 span of Y-axis is 25 counts.

reported that NdOOH crystals deposited on the cathode surface by an electrolysis operation in the NaOH -0.3 mol% $\text{Nd}(\text{OH})_3$ mixture melt at 400°C [24], and that NdOOH was synthesized from Nd_2O_3 - H_2O system by keeping a pressure of 20 MPa at 500°C for 120 h [25]. In the XRD patterns of mechanochemical products obtained by a milling, since these peaks at 16° and 22° were observed small as shown in **Figures 2(c), (d), 4(a), (b), (e) and (f)**, it was thought that NdOOH generated from $\text{Nd}(\text{OH})_3$ contained in the Nd_2O_3 reagent. The NdOOH was chlorinated with CCl_4 to NdOCl with the chlorination of Nd_2O_3 to NdOCl by a mechanochemical reaction, since the peaks of NdOOH was not observed in the XRD patterns of products obtained on sufficient chlorination conditions. Since it was suggested according to the sulfurization of TiO_2 or $\text{Ti}(\text{OH})_4$ with CS_2 to Ti_3S_4 that the reaction temperature of $\text{Ti}(\text{OH})_4$ was lower than that of TiO_2 [26], the chlorination of $\text{Nd}(\text{OH})_3$ with CCl_4 to NdOCl might be easier to be chlorinated than that of Nd_2O_3 .

The Raman spectra of the milled Nd_2O_3 and NdOCl powders show in **Figures 9(b) and (e)**, and the large difference were not observed in comparison with those of the powders before the milling treatment. However, in the milled raw Nd_2O_3 reagent which a generation of

NdOOH was confirmed by a XRD analysis, the peak was observed at 325 cm^{-1} in the Raman spectrum as shown in **Figure 9(c)**. This peak was considered to be identified the peak of NdOOH at 339 cm^{-1} [27], and it was presumed that the peak shifted by a residual stress after the milling treatment. This peak at 325 cm^{-1} was also observed also in the spectra of mechanochemical products as shown in **Figures 3(b), (c), 5(a), (b) and (n)**. On the other hand, the Nd_2O_3 peak of the dry Nd_2O_3 powder was observed a shift to 425 cm^{-1} from 433 cm^{-1} after the milling treatment as shown in **Figure 9(b)**.

As for the peak shift of Raman spectra, the most of NdOCl spectrum peaks in the products obtained in our mechanochemical experiments were shifted to lower wavenumbers than those of tetragonal NdOCl crystals [19], and they were considered to be influence of the residual stress by a milling as described above sections. According to the Raman spectroscopy measurements of Cr_2O_3 thin films [28], Y_2O_3 - ZrO_2 barrier coatings [29], epitaxial GaN layers [30], and Al_2O_3 single crystals [31], in the state where the stress was applied, the redshift which the peak shifted to low wavenumbers was based on the tensile stress, and the tensile stress remained in the surface of products which obtained by using a planetary ball mill. Therefore, the large compressive force of the level on which the tensile stress remained in the products was loaded on particles during our mechanochemical experiments, and contributed to progress of the chlorination to NdOCl from Nd_2O_3 with CCl_4 .

3.9. Relevant Milling Condition for Chlorination to NdOCl

In the present study, most mechanochemical experiments were carried out using a zirconia pot and balls in various milling conditions, such as milling time, molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$, number of ball, and revolution speed. It was confirmed in the Section 3.6 that the chlorination to NdOCl progressed with an acceleration of the revolution speed.

From the XRD patterns and Raman spectra of mechanochemical products, we examined the relevant milling time, molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$, and number of ball for the effective chlorination to NdOCl from Nd_2O_3 with CCl_4 . The NdOCl peaks in XRD patterns of products of run-5, -6, -7, -10, -11, -12, -13, and -14 exists as shown in **Figure 4**, and the NdOCl peaks in their Raman spectra from run-4 to run-14 except run-12 exists in **Figure 5**. Although the relevant conditions are that all added Nd_2O_3 powders in a pot react with CCl_4 , it is also necessary to not be worsened the crystal structure of products and to decrease the residual stress of products by milling operation. The crystal structure is worsened to fine particles by a milling operation, and the peaks of XRD pattern shows broad as shown in **Figure 8**. When the residual

tensile stress increases, the characteristic Raman peak shifts to lower wavenumber as described in section 3.8. Thus, the peak width in a XRD pattern and the peak shift of a Raman spectrum can be used as the index which examines a relevant condition. The peak width in a XRD pattern was estimated using a full width at half maximum, FWHM, of (1,0,1), (1,1,0), and (1,0,2) peaks. The Raman shift, $\Delta\nu$, was calculated the deference with the wavenumber in Raman peak-I at 119.4 cm^{-1} , peak-II at 180.7 cm^{-1} , peak-III at 349.1 cm^{-1} , and peak-IV at 461.0 cm^{-1} of the dry NdOCl powder as shown in **Figure 9(d)**.

Figure 10 shows the change of FWHM of XRD peaks and $\Delta\nu$ of Raman peaks by the milling time in the case of $10\text{ mm}\phi \times 16$ balls and molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3 = 3.47$ in a zirconia pot. The FWHM values of XRD peaks decrease with an increase of milling time, and the $\Delta\nu$ values of Raman peaks in 2 h is smaller than those in 1 or 4 h. Since the difference of FWHM values in between 2 and 4 h are small, it is thought that the chlorination to NdOCl was completed in 2 h and then it is presumed that the distortion was given to the produced NdOCl powder by milling operation. The change of FWHM and $\Delta\nu$ by the molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ in the case of $10\text{ mm}\phi \times 16$ balls in a zirconia pot for 2 h is shown in **Figure 11**. When the molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ increased, the FWHM values increased and the $\Delta\nu$ values were more negative. As described in the section 3.4, it is thought that the molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3 = 3.47$ was enough to synthesize NdOCl . As for the change of FWHM and $\Delta\nu$ by the number of $10\text{ mm}\phi$ balls in a zirconia pot in the milling

case of the molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3 = 3.47$ for 2 h, the FWHM and $\Delta\nu$ values by milling with 16 balls are smaller than the other conditions as shown in **Figure 12**. However, the $\Delta\nu$ shows scattered values in milling with 8 or 24 balls. This reason is thought that the chlorination to NdOCl was not completed, because the milling with 8 balls was not enough to obtain the required energy for chlorination to NdOCl and the milling with 24 balls restrained the motion of balls in a pot. Therefore, the relevant milling conditions for chlorination to NdOCl from 0.4 g of Nd_2O_3 with CCl_4 in a zirconia pot at 500 rpm is selected that the milling time is 2 h, the molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ is 3.47, and the number of balls is 16.

4. Conclusions

In the present study, the chlorination from Nd_2O_3 with CCl_4 was carried out using a planetary ball mill, and the products were estimated by the XRD analysis and Raman spectroscopy. The obtained results are as follows.

It was confirmed that the chlorination to NdOCl from Nd_2O_3 with CCl_4 was advanced at room temperature by the mechanochemical method. However, NdCl_3 could not be synthesized in this mechanochemical study. The products obtained by a milling in a zirconia or tungsten carbide pot were pale purple colored NdOCl . But NdOCl was not produced by a milling in a SUS304 pot. An extension of the milling time, an increase of the number of ball, an acceleration of the revolution speed, and the selection of the pot made of a high density material were

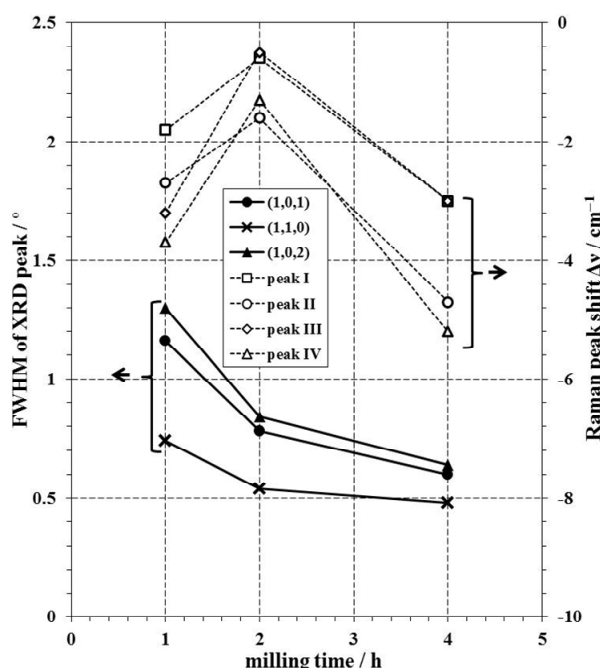


Figure 10. Change of FWHM of XRD peaks and $\Delta\nu$ of Raman peaks by milling time in case of $10\text{ mm}\phi \times 16$ balls and molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3 = 3.47$ in a zirconia pot.

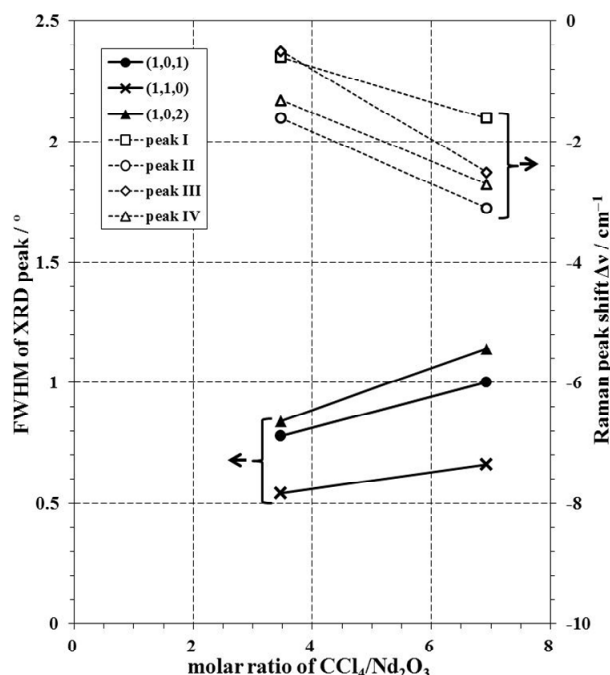


Figure 11. Change of FWHM of XRD peaks and $\Delta\nu$ of Raman peaks by molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ in case of $10\text{ mm}\phi \times 16$ balls for 2 h milling in a zirconia pot.

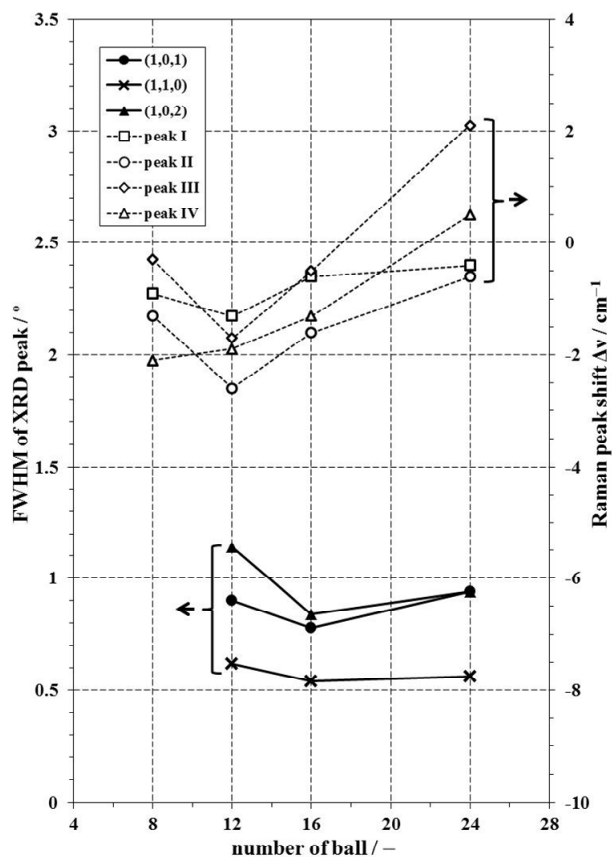


Figure 12. Change of FWHM of XRD peaks and $\Delta\nu$ of Raman peaks by number of 10 mm ϕ balls in case of molar ratio of $\text{CCl}_4/\text{Nd}_2\text{O}_3$ for 2 h milling in a zirconia pot.

effective for the chlorination to NdOCl from Nd_2O_3 with CCl_4 . NdOOH was generated from $\text{Nd}(\text{OH})_3$ of impurity contained in Nd_2O_3 reagent by a milling, and this NdOOH was chlorinated with CCl_4 to NdOCl by a mechanochemical reaction. It was confirmed that tensile stress remained in the milled powder by using a planetary ball mill.

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