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CHARACTERIZATION OF NEODYMIUM TRICHLORIDE HYDRATES AND NEODYMIUM HYDROXYCHLORIDE

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Summary

Neodymium trichloride hexahydrate ($NdCl_3.6H_2O$) was dehydrated by heating it in either air, argon, HCl or argon–HCl mixtures to germinate the intermediate species. The hexahydrate ($NdCl_3.6H_2O$) was found to decompose to pentahydrate ($NdCl_3.5H_2O$) which in turn decomposed to tetrahydrate ($NdCl_3.4H_2O$). The latter decomposed to monohydrate ($NdCl_3.H_2O$) as the dehydration proceeded towards anhydrous $NdCl_3$. Simultaneously to dehydration, formation of neodymium oxychloride (NdOCl) and neodymium hydroxychloride ($Nd(OH)_2Cl$) took place. $Nd(OH)_2Cl$ was isolated and characterized by X-ray diffraction. Its decomposition temperature was determined to be 376 °C by differential thermal analysis. Its heat of decomposition to NdOCl and H_2O was determined by differential scanning calorimetry to be 23 479 cal mol^{-1} (98 283 J mol^{-1}). Its density was found to be 4.596 g cm^{-3} at 25 °C.

1. Introduction

Neodymium trichloride is one of the most important compounds of neodymium metal. It is used as feed material in the electrolytic process for the production of neodymium metal. The chloride is readily available in its hydrated form ($NdCl_3.6H_2O$), but prior to using it in the electrolytic cell, it must be dehydrated.

The $NdCl_3.6H_2O$ was supplied as a cast and its differential thermal analysis (DTA) trace is shown in Fig. 1. The peaks labeled A, B, C, D, E and F in Fig. 1 correspond to specific intermediate products. Peak A corresponds to $NdCl_3.6H_2O$ and peak F corresponds to the melting of anhydrous $NdCl_3$. The DTA curve of pure anhydrous $NdCl_3$ is shown in Fig. 2. No peak other than the melting peak is observed. Figures 3 and 4 show the DTA curves of supposedly "anhydrous" $NdCl_3$ from two suppliers. Clearly both figures indicate incomplete dehydration of the products.

Previous investigators [1, 2], on the basis of weight loss during the dehydration, have concluded that peak B in Fig. 1 corresponds to trihydrate ($NdCl_3.3H_2O$), peak C to dihydrate ($NdCl_3.2H_2O$) and peak D to monohydrate

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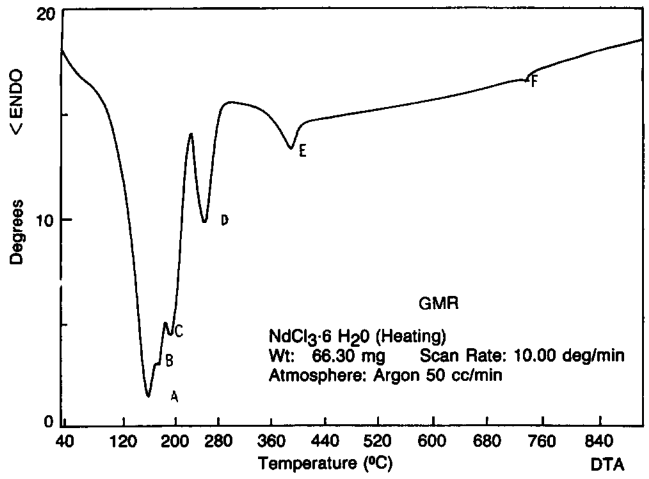

Fig. 1. DTA curve of $NdCl_3.6H_2O$.

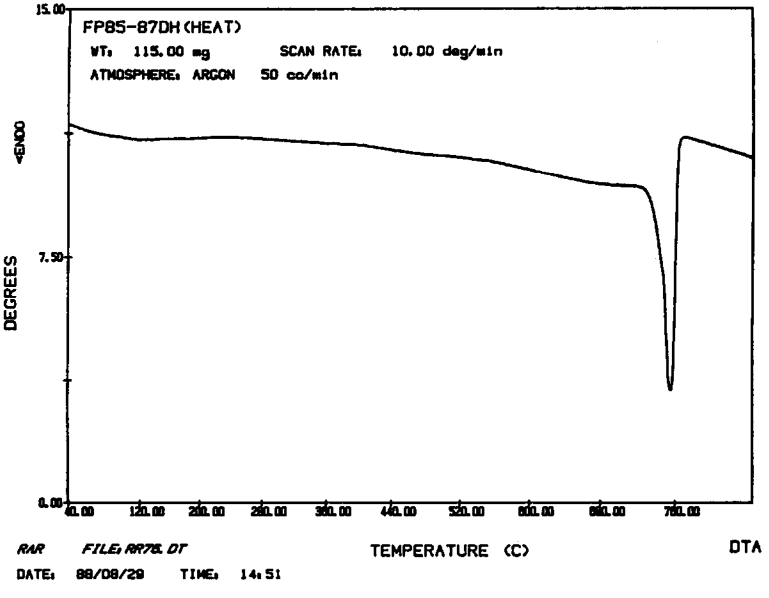

Fig. 2. DTA curve of anhydrous pure $NdCl_3$.

($NdCl_3.H_2O$). As for peak E, it was speculated to be due to "occluded" water. It should be noted that the trihydrate and dihydrate have never been prepared and characterized by X-ray diffraction (XRD).

Weight loss measurements alone cannot establish the formulae of intermediate products of dehydration, particularly when the products have a very narrow temperature range of existence, as is the case for intermediates in the $NdCl_3.6H_2O$ dehydration [3, 4]. Figure 5 shows the TGA curve of $NdCl_3.6H_2O$.

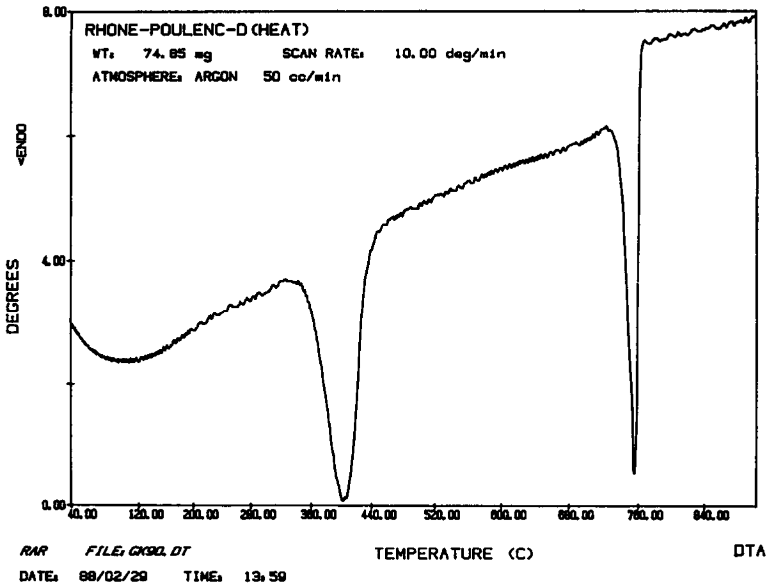

Fig. 3. DTA curve of "anhydrous" $NdCl_3$ from Rhône-Poulenc.

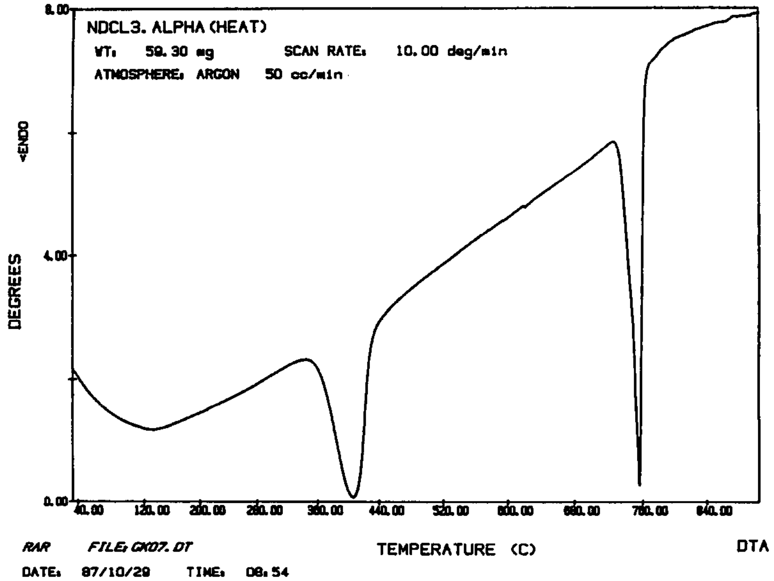

Fig. 4. DTA curve of "anhydrous" $NdCl_3$ from ALFA.

A total weight loss of 46.31 wt.% is observed and this is well in excess of the 30.17 wt.% which is expected from stoichiometric considerations. Thus speculations based on the weight loss measurements alone can be very misleading. Established practice in thermal analysis methods allows us to state safely that compounds corre-

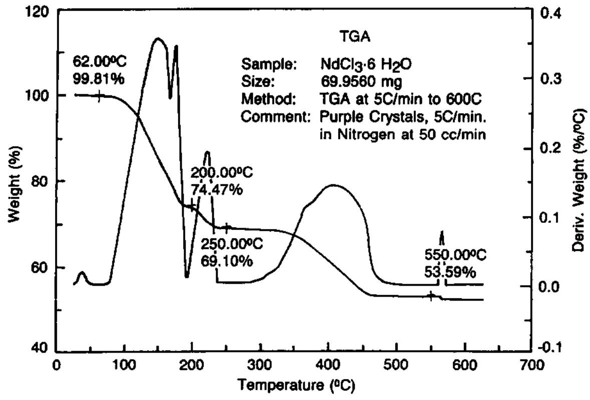

Fig. 5. TGA curve of $NdCl_3.6H_2O$.

sponding to peaks D, E and F are quite stable in the temperature range of existence. This is so because they are separated by well-pronounced plateaux in the weight loss (%) *vs.* temperature curve. It is apparent from the analysis above, that heating the hexahydrate to a temperature of about 430 °C will result in the maximum weight loss and thus remove all the water of crystallization.

The fact that both DTA and thermogravimetric analysis (TGA) curves were obtained under inert atmospheres indicates that any hydrolysis taking place simultaneously with the dehydration is autogeneous, *i.e.* is caused by the water evolving during dehydration. Such hydrolysis may be described by the reaction

$$NdCl_3 + H_2O \rightarrow NdOCl + 2HCl \qquad (1)$$

and it may be accompanied by the reaction

$$NdCl_3 + \tfrac{1}{2}O_2 \rightarrow NdOCl + Cl_2 \qquad (2)$$

in the presence of oxygen during the dehydration.

Occurrence of reactions (1) and (2) was verified by the evolution of HCl and Cl_2 during dehydration.

The standard free energy changes of reactions (1) and (2), calculated using the data given in refs. 5–7, are plotted as a function of temperature in Fig. 6. The data indicate that reactions (1) and (2) should proceed under standard states of the reactants and products. In the dehydration of the chloride in an inert atmosphere, the activity of water because of H_2O present as water of hydration is likely to be quite high and that of HCl should be negligible. Under these conditions, reaction (1) is more favorable to proceed than when under standard conditions. Similar arguments may be advanced for reaction (2) in the presence of oxygen and absence of chlorine in the dehydration atmosphere.

The present study was undertaken with the purpose of identifying and characterizing the intermediate lower hydrates and any compound formed during the dehydration of $NdCl_3.6H_2O$ by combining thermal analysis and X-ray diffraction techniques.

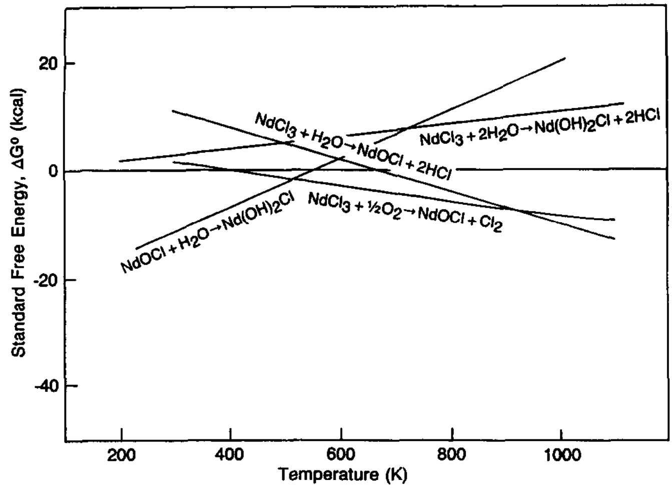

Fig. 6. Standard free energy change $\Delta G°$ of reactions relevant to dehydration *vs.* temperature.

2. Experimental details

2.1. Materials

Cast $NdCl_3.xH_2O$ (47 wt.% rare earth equivalent) typically containing 66.5 wt.% $NdCl_3$, was used. High purity HCl (99.9%) and argon (99.999%) were used for atmospheres for drying in this study.

2.2. Apparatus

Initial dehydration was conducted in a drying oven equipped with a motor for air circulation and connected to a fume hood for venting.

Dehydration in argon and/or HCl streams was conducted in the apparatus shown schematically in Fig. 7. It consisted of a closed silica container (7 cm outside diameter) by 65 cm deep by 0.2 cm wall thickness) fitted with gas inlet and outlet ports. An alumina sparge tube (0.6 cm outside diameter by 76 cm long by 0.15 cm wall thickness) was used to bubble the gases through the salt, while a mass flow controller and a dual tube mixing rotameter were used to regulate the HCl and argon flow rates respectively. A tubular clamshell heating element furnace (7.5 cm inside diameter by 46 cm long) regulated by means of a programmable temperature controller was used to heat the reactor. The temperature was monitored by a calibrated thermocouple positioned adjacent to the furnace wall at mid-salt level.

2.3. Procedures

Dehydration of $NdCl_3.6H_2O$ in air was used as a method of preparing the intermediate hydrates and compounds. A preweighed amount of the hexahydrate was spread onto the surface of an aluminum pan. The pan was placed in the drying oven initially set at 80 °C. The temperature was increased manually, while the weight loss was periodically monitored by weighing the aluminum pan and its

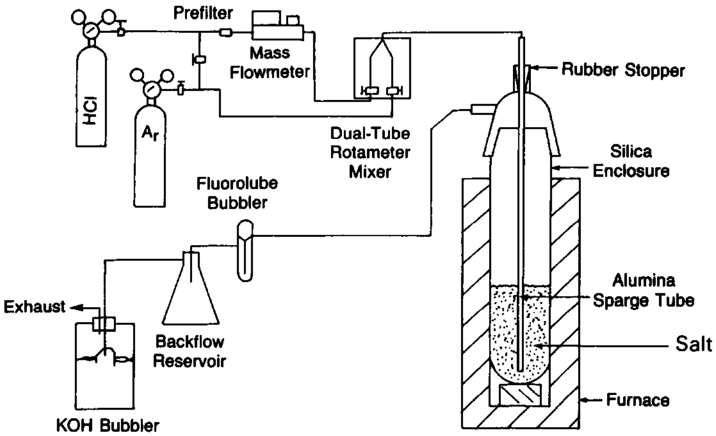

Fig. 7. Schematic diagram of the apparatus for dehydration in argon–HCl.

content. After each weighing, the salt was stirred thoroughly to replenish the surface. By varying temperature and time of dehydration, material was prepared in which certain peaks in the DTA curve of Fig. 1 were not observed. At the end of each experiment, the dried material was transferred into a drybox and ground. A sample was placed in a special sample fixture covered with mylar film to avoid hydrolysis and analyzed by XRD. Another sample was analyzed by DTA. Approximately 100 mg of the salt were placed in a platinum crucible and heated at 10 °C min^{-1} under an argon flow of 50 ml min^{-1}. Alumina was used as a reference material. A sample (69 mg) was heated at 5 °C min^{-1} in nitrogen at 50 ml min^{-1} in TGA.

Elemental chemical analyses (neodymium, chlorine, rare earth) were performed on the samples via wet chemical techniques. The oxygen content in each of the samples, for estimating the amount of NdOCl, was determined using the LECO oxygen determinator. The HCl treatment of $Nd(OH)_2Cl$ was studied under the conditions of dehydration. The silica container, schematically shown in Fig. 7, was loaded in a drybox with a preweighed amount of salt. The assembly was taken out of the drybox, positioned in the furnace and hooked up to the gas lines. Dehydration was conducted using either an argon, an argon–HCl or an HCl stream at a flow rate of 100 ml min^{-1} and at temperatures of 300 or 400 °C. Condensation of the evolving H_2O on the cold part of the glass apparatus was prevented by use of a heating gun. At the end of the experiment the apparatus was cooled to room temperature and transferred into a drybox where the salt was weighed to determine any weight change, and samples were collected for characterization.

3. Results and discussion

3.1. Identification of lower hydrates

The experimental conditions for the preparation of partially dehydrated products are described in Table 1. The DTA curve of the product of batch 1,

TABLE 1

Experimental conditions of partial dehydration

Batch	T_{max} (°C)	*Total time* (h)	*Initial weight* (g)	*Weight loss* (g)	*XRD results (major phase)*
1	230	3.5	865	249 (28.8%)	$Nd(OH)_2Cl$
2	145	61	715	212 (29.7%)	$NdCl_3.H_2O$
3	93	17	593	99 (16.8%)	$NdCl_3.4H_2O$
4	100	6	593	108 (18.3%)	$NdCl_3.5H_2O$

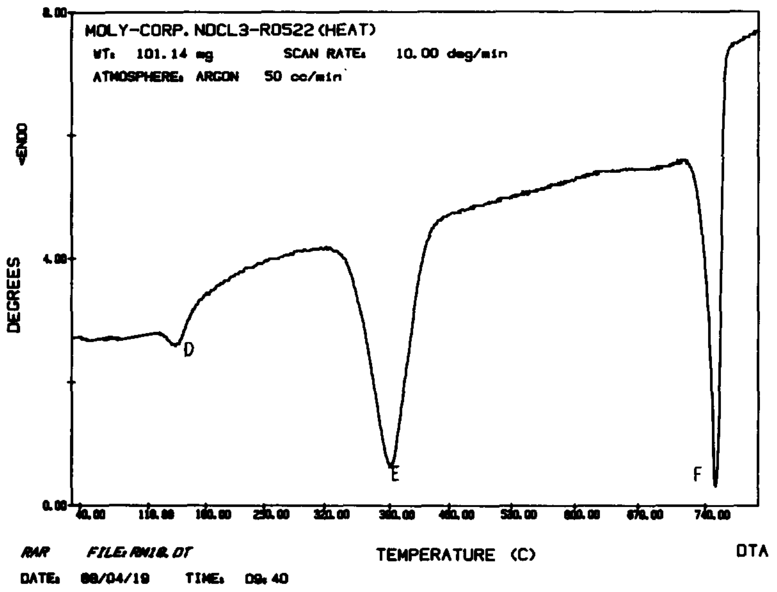

Fig. 8. DTA curve of batch 1.

Table 1, is shown in Fig. 8. This curve resembles those of Figs. 3 and 4 where only peaks E and F (Fig. 1) appear. Analysis by XRD showed the predominance of $NdCl_3$. The salt was dissolved in H_2O and the residue was thoroughly washed with H_2O and dried in an oven at 130 °C for 1 h. Figure 9 shows the DTA curve of the residue. It consists of only one peak, that corresponding to peak E (Fig. 1). Noticeable is the absence of peak F (Fig. 1) which is attributed to the melting of $NdCl_3$. The X-ray powder diffraction pattern of the residue is shown in Fig. 10. A very good match exists between the pattern shown in Fig. 10 and that of the $Nd(OH)_2Cl$, as described in the literature [8]. This compound had been synthesized previously [8] by the reaction of Nd_2O_3 with aqueous $FeCl_3$ solutions in titanium inserts enclosed in stainless steel autoclaves at temperatures between 500 and 600 °C, but no one has reported its formation during dehydration of

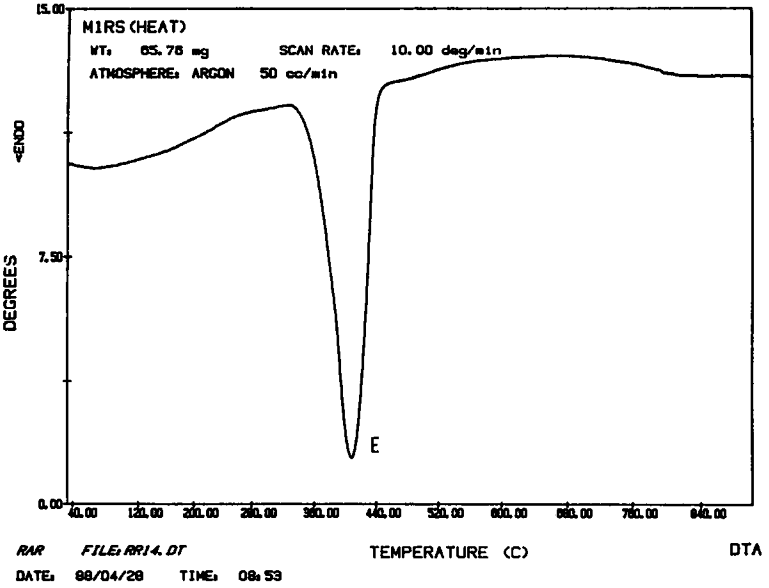

Fig. 9. DTA curve of $Nd(OH)_2Cl$.

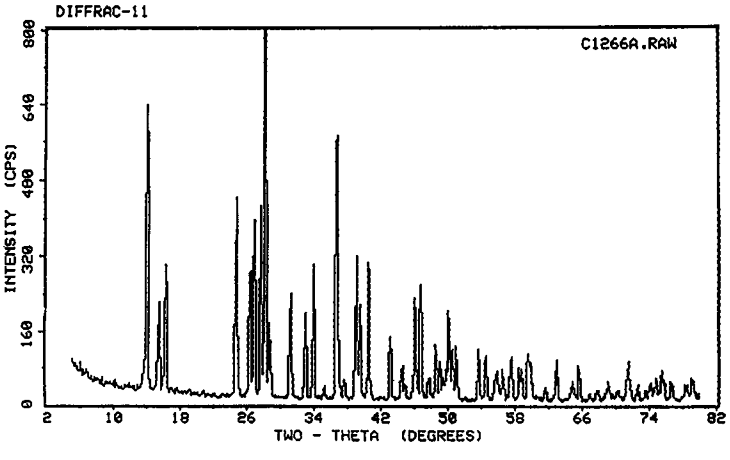

Fig. 10. XRD diffraction pattern of $Nd(OH)_2Cl$.

$NdCl_3.6H_2O$. However, formation of $Nd(OH)_2Cl$ during the dehydration may occur by the reaction

$$NdCl_3 + 2H_2O \rightarrow Nd(OH)_2Cl + 2HCl \qquad (3)$$

The absence of the $Nd(OH)_2Cl$ melting peak in Fig. 9 may be explained by the decomposition reaction

$$Nd(OH)_2Cl \rightarrow NdOCl + H_2O \qquad (4)$$

according to which NdOCl forms and H_2O evolves. The melting point of NdOCl lies outside the temperature range shown in Fig. 9. XRD examination of the product from the decomposition of $Nd(OH)_2Cl$ confirmed the NdOCl formation. However, the characterization of $Nd(OH)_2Cl$ will be given later.

Batch 2 in Table 1 resulted in a product whose DTA curve is shown in Fig. 11. Three peaks, D, E, and F are present. The XRD pattern of this product matched the XRD powder diffraction pattern of $NdCl_3.H_2O$ (3-139 card in the Joint Committee on Powder Diffraction Standards 1974). As shown in Table 1, this product was obtained under conditions leading to a total weight loss of 29.7 wt.% which compares well to the stoichiometric weight loss (30.17 wt.%) corresponding to anhydrous $NdCl_3$. This is an additional proof that the weight loss alone, in the presence of hydrolysis, cannot be considered as a guide to successful dehydration. Most of the previous investigators failed to recognize this.

In batch 3, Table 1, conditions were created that gave predominance to peak C as shown in Fig. 12 which is the DTA curve for the product of this dehydration experiment. The X-ray powder diffraction pattern of this product confirmed that the major phase is $NdCl_3.4H_2O$ (3-84 card in the Joint Committee on Powder Diffraction Standards 1974).

Finally, batch 4, in Table 1, resulted in a product in which the peak B is the most predominant, as shown in Fig. 13. The X-ray powder diffraction pattern of this product confirms that the major phase corresponds to the powder pattern of $NdCl_3.5H_2O$ (3-77 card in the Joint Committee on Powder Diffraction Standards 1974).

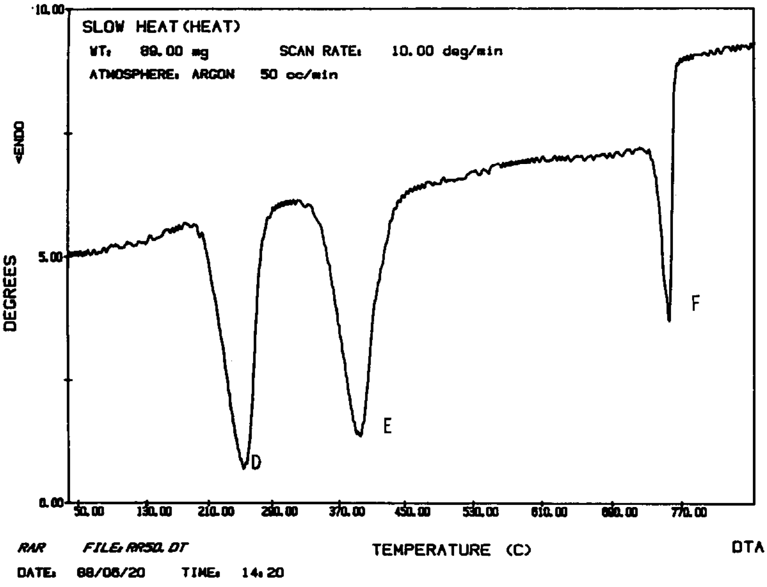

Fig. 11. DTA curve of a mixture consisting of $NdCl_3.H_2O$-$Nd(OH)_2Cl$-$NdCl_3$.

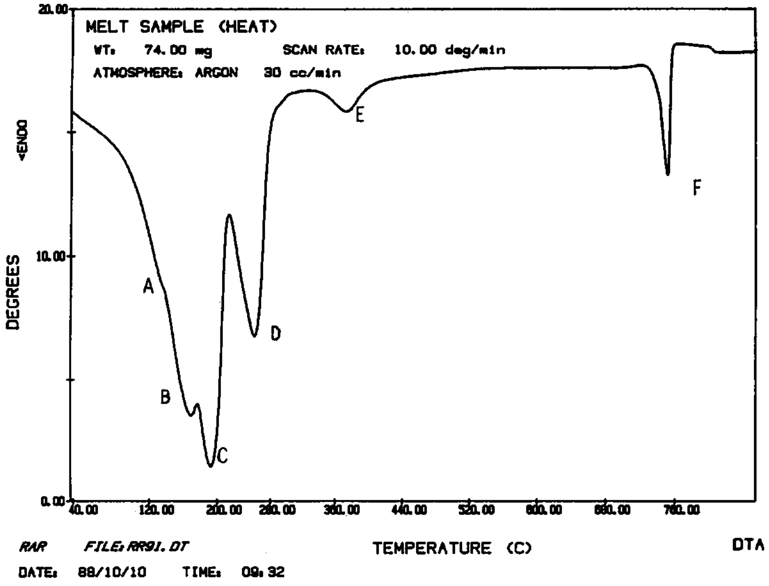

Fig. 12. DTA curve of a mixture containing predominately $NdCl_3.4H_2O$.

According to the above experimental findings the dehydration of $NdCl_3.6H_2O$ proceeds as follows:

$$NdCl_3.6H_2O \rightarrow NdCl_3.5H_2O + H_2O \tag{5}$$

$$NdCl_3.5H_2O \rightarrow NdCl_3.4H_2O + H_2O \tag{6}$$

$$NdCl_3.4H_2O \rightarrow NdCl_3.H_2O + 3H_2O \tag{7}$$

$$NdCl_3.H_2O \rightarrow NdCl_3 + H_2O \tag{8}$$

Simultaneous with the dehydration reactions (5)–(8), reactions (1)–(4) also take place resulting in contamination of the anhydrous $NdCl_3$ with NdOCl.

3.2. Characterization of $Nd(OH)_2Cl$

3.2.1. Preparation of $Nd(OH)_2Cl$

$Nd(OH)_2Cl$ was isolated by dissolution of $NdCl_3$, contaminated with hydroxychloride, in H_2O. $NdCl_3$ containing $Nd(OH)_2Cl$ was prepared by partial dehydration of the $NdCl_3.6H_2O$ in air at temperatures lower than 250 °C and times necessary to remove all the water of crystallization. Under these conditions, the partially dehydrated salt contained mainly $NdCl_3$, $Nd(OH)_2Cl$ and a small amount of NdOCl.

The hydroxychloride formed a residue which was filtered out, washed thoroughly with H_2O and dried in an oven at 130 °C for 1 h. Several batches of $Nd(OH)_2Cl$ were prepared. Table 2 presents the results of chemical analysis of typical samples of $Nd(OH)_2Cl$. The results are in agreement, within analytical error, with the expected formula weights.

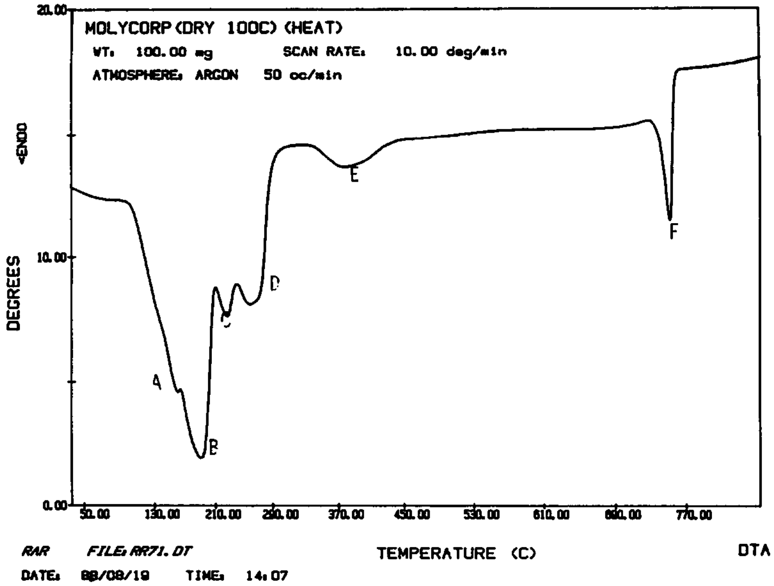

Fig. 13. DTA curve of a mixture containing primarily $NdCl_3.5H_2O$.

TABLE 2

Chemical analysis of $Nd(OH)_2Cl$ samples

Sample	*Neodymium*	*Prasedymium*	*Chlorine*	*Oxygen*
1	65.9	0.5	16.3	17[a]
2	63.6	0.4	14.5	14
formula weight	67.5		16.6	14.9

[a] Less accurate due to double oxygen peaks.

3.2.2. Density measurements

Density was measured by a pycnometer using octoil ($C_6H_4(COOC_8H_{17})_2$) as the reference liquid. As a first step, the density of the octoil was determined using water as a reference liquid. The density of the octoil was found to be 0.97964 cm^{-3} which compares well with the value of 0.98 g cm^{-3} reported by the supplier. Hydroxychloride appears to be insoluble in octoil. Prior to the final density measurement, the bottle containing the sample powder and the octoil liquid was placed in a vacuum bell to remove absorbed gases. A weighed sample of 4.91774 g of hydroxychloride displaced 1.04833 g of octoil. This gave a density of 4.596 g cm^{-3}.

According to the literature [8], the lattice volume of the unit cell is 150 Å^3 for $Nd(OH)_2Cl$. Assuming two formula units per unit cell for $Nd(OH)_2Cl$ [9], the theoretical density is calculated to be 4.73 g cm^{-3}. The experimentally determined value is in agreement with the calculated theoretical value, within experimental error (± 2.8%).

3.2.3. Decomposition weight loss

A sample of $Nd(OH)_2Cl$, weighing 103 mg, was decomposed under argon in the DTA equipment. A decomposition weight loss of 8 mg was observed which corresponds to 7.7 wt.% and compares well with the expected formula weight loss of 8.4 wt.% by reaction (4).

3.2.4. Heat of decomposition and calculation of thermodynamic data

The heat of decomposition was determined by differential scanning calorimetry (DSC). DSC measurements were performed on samples of approximately 5 mg contained in aluminum crucibles heated at 10 °C min^{-1} in argon, 50 ml min^{-1}. The heat of dissociation is given by the area under the DSC curve and is automatically calculated by the instrument which gives a calories per gram factor for each sample. Multiplication by the molecular weight results in the determination of the heat of dissociation in kilocalories per mole. The instrument was calibrated by determining the heat of fusion of indium metal which was found to be 0.80 kcal mol^{-1}. This value agrees well with the published value of 0.78 ± 0.02 kcal mol^{-1} [10].

$Nd(OH)_2Cl$ is presumed to decompose according to reaction (4). Figure 14 shows the DSC curve for a sample of $Nd(OH)_2Cl$ weighing 5.35 mg. The heat of decomposition determined by this technique on several $Nd(OH)_2Cl$ samples gave an average value of 23 479 cal mol^{-1} (98 285 J mol^{-1}).

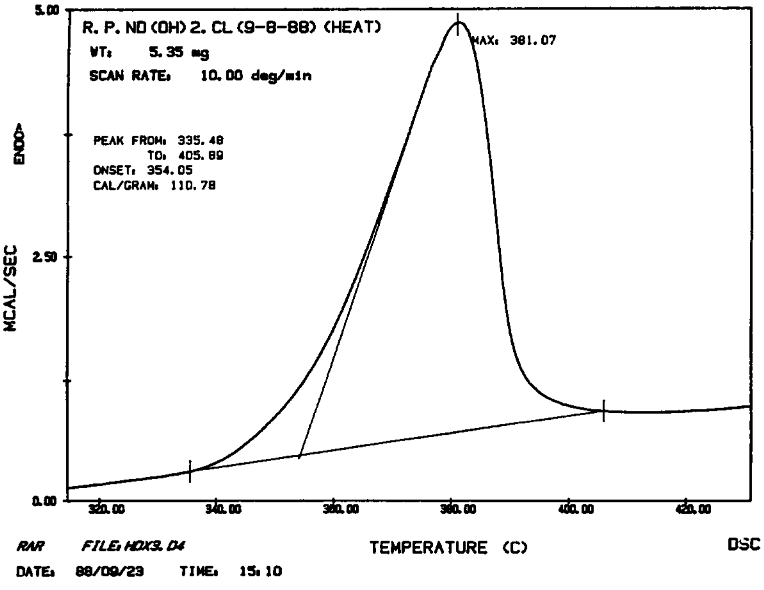

Fig. 14. DSC curve of $Nd(OH)_2Cl$.

Using the measured value of the heat of decomposition for $Nd(OH)_2Cl$ and estimated values [11] for the entropy of formation, the standard free energy change for the reaction

$$NdOCl + H_2O \rightarrow Nd(OH)_2Cl \tag{9}$$

was calculated (Appendix A) and is given by

$$\Delta G^\circ_{(9)} = -23\,479 + 40.906T \tag{10}$$

The standard free energy of reaction (3) was also estimated (Appendix A), by combining reactions (1) and (9), and is given by

$$\Delta G^\circ_{(3)} = -1088 + 10.596T \tag{11}$$

It is plotted *vs.* temperature in Fig. 6 and shows that formation of $Nd(OH)_2Cl$ via reaction (3) is thermodynamically unfavorable at all temperatures under standard states of the reactants and products. However, this reaction may proceed to some extent because of the negligible pressure of HCl in the atmosphere. However, the standard free energy change for reaction (4) is negative below 350 °C and, therefore, $Nd(OH)_2Cl$ is likely to form below this temperature and decompose above this temperature. In this case, $Nd(OH)_2Cl$ and NdOCl are likely to be in their standards states and the activity of water can also be presumed to be high as explained earlier.

3.2.5. HCl treatment of Nd(OH)$_2$Cl

The HCl treatment of $Nd(OH)_2Cl$ was studied using the apparatus shown in Fig. 7. A small amount (about 67 g) of $Nd(OH)_2Cl$ was treated at 300 °C for 4 h

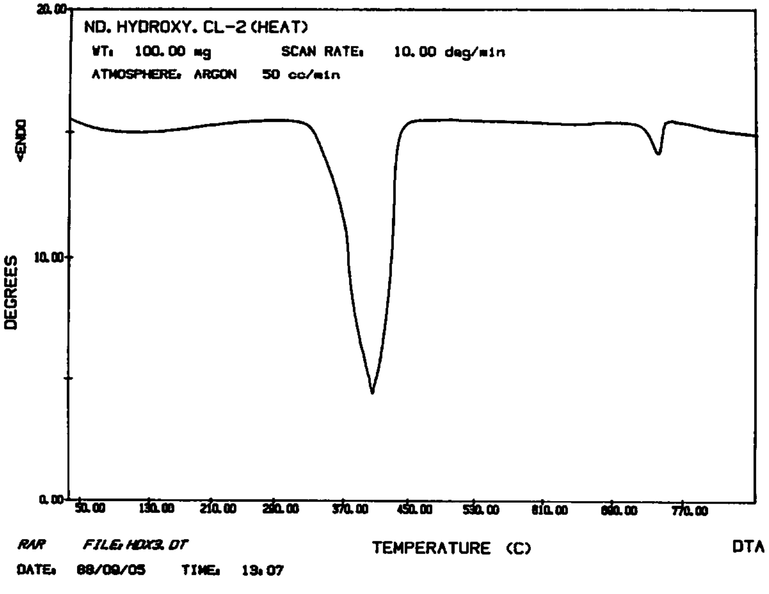

Fig. 15. DTA curve of $Nd(OH)_2Cl$ after treatment with HCl at 300 °C.

with HCl (flow rate 200 ml min^{-1}). Only a small increase in weight (0.9 g) occurred and the DTA curve of the product, shown in Fig. 15, indicates that the $Nd(OH)_2Cl$ was unaffected. The small amount of $NdCl_3$ formed was probably due to the conversion of any free NdOCl which was present in the sample. This means that the presence of HCl during dehydration cannot prevent the formation of $Nd(OH)_2Cl$.

In another experiment, the hydroxychloride was first decomposed by heating to 430 °C and then treated with HCl as above. The result was a very high purity $NdCl_3$ containing 0.06 wt.% O. Therefore, high purity anhydrous $NdCl_3$ can be prepared by first heating the hexahydrate to 430 °C and then treating the product with HCl at 300 °C.

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Appendix A: Estimation of thermodynamic data

(1) Standard entropy S°_{298} for $Nd(OH)_2Cl$ was calculated by Latimer's method [11] using S°_{298} for Nd^{3+} = 13.9 cal K^{-1}, OH^- = 3.0 cal K^{-1} and Cl^- = 6.0 cal K^{-1}. It was found to be 26.8 cal K^{-1} mol^{-1}.

(2) Standard entropy of formation ΔS°_{298} for $Nd(OH)_2Cl$ was calculated from the reaction

$$NdOCl + H_2O \rightarrow Nd(OH)_2Cl \qquad (9)$$

using S°_{298} for $Nd(OH)_2Cl = 26.8$ cal K^{-1} mol^{-1} from above, $NdOCl = 22.6$ cal K^{-1} mol^{-1} [10] and $H_2O = 45.016$ cal K^{-1} mol^{-1} [10]. It was found to be -40.906 cal K^{-1} mol^{-1}.

(3) Standard free energy change ΔG° for reaction (9) was calculated by using the relation

$$\Delta G^\circ = \Delta H^\circ_{298} - T\Delta S^\circ_{298} \qquad (12)$$

The value of ΔH°_{298} was found equal to $-23\,479$ cal mol^{-1} by DSC reported earlier.

$$\Delta G^\circ_{(9)} = -23\,479 + 40\,906T$$

(4) Standard free energy change, ΔG° for the following reaction:

$$NdOCl + H_2O \rightarrow Nd(OH)_2Cl + 2HCl \qquad (13)$$

was calculated from the values of ΔG° of reaction (9) and reaction (1). Reaction (13) is the sum of reactions (9) and (1) so ΔG° for this reaction is given by the equation

$$\Delta G^\circ_{(3)} = -1088 = 10.596T \qquad (11)$$