

## Hydrothermal equilibria in $\text{Nd}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system

T R NARAYANAN KUTTY, M N VISWANATHIAH\* and  
J A K TAREEN\*

Department of Inorganic and Physical Chemistry, Indian Institute of Science,  
Bangalore 560 012

\*Mineralogical Institute, Manasa Gangotri, Mysore 570 006

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**Abstract.** Isobaric equilibria in  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O-CO}_2$  system have been determined at 1500 atmospheres and temperature range of 200–900°C. The mole fraction of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the fluid phase were varied from 0.0 to 1.0. The stable phases are  $\text{Nd}(\text{OH})_3$ -hexagonal,  $\text{Nd}(\text{OH})\text{CO}_3$ -hexagonal,  $\text{Nd}_2\text{O}_3\text{CO}_3$ -hexagonal and  $\text{NdOOH}$ -monoclinic.  $\text{Nd}(\text{OH})_3$  is stable only when  $X_{\text{CO}_2}$  is less than 0.008. The stability field of  $\text{Nd}(\text{OH})_3$  extends parallel to temperature axis. Thus,  $\text{Nd}(\text{OH})_3$  coexists with all the other phases. When  $X_{\text{CO}_2} = 1.0$ , the only stable phase is  $\text{Nd}_2\text{O}_3\text{CO}_3$ -hexagonal.

**Keywords.** Hydrothermal equilibria; rare earth carbonates.

### 1. Introduction

In the ternary heterogeneous system:  $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$  ( $\text{Ln} = \text{Lanthanides}$ ), several solid phases have been reported, based on the experiments carried out at temperatures below 100°C and total pressure of 1 atm. (Dexpert *et al* 1972; Turcotte *et al* 1969). A few of the hydroxycarbonates, in this system, are reported to be isostructural with minerals like bastnaesite, ancyllite, lanthanite and tenerite. The only hydrothermal investigation in  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O-CO}_2$  system is by Christensen (1973) who identified  $\text{Nd}(\text{OH})_3$ ,  $\text{Nd}_2\text{O}_3\text{CO}_3$  and  $\text{Nd}(\text{OH})\text{CO}_3$  as the stable phases. However, no quantitative data are presented by Christensen (1973), since he was interested mainly in the crystallographic aspects of the phases formed. This paper deals with the isobaric equilibria studies with  $\text{Nd}_2\text{O}_3$  at various mole fractions of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  under a total pressure of 1500 atm.

### 2. Experimental

$\text{Nd}_2\text{O}_3$  of 99.9% purity (Fluka A G Switzerland) is used. In order to develop known partial pressures of water and  $\text{CO}_2$ , we have used oxalic acid dihydrate, anhydrous oxalic acid and silver oxalate as source materials. Known quantities of these, when mixed in different proportions could generate varying mole fractions of  $\text{CO}_2(X_{\text{CO}_2})$  in the fluid phase. ( $X_{\text{CO}_2} = M_{\text{CO}_2}/M_{\text{CO}_2} + M_{\text{H}_2\text{O}}$ , where  $M_{\text{CO}_2}$  and  $M_{\text{H}_2\text{O}}$  are the number of moles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively). Oxalic acid decomposes above 120°C, under pressure as:  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 2\text{H}_2\text{O} + 2\text{CO}_2 + \text{H}_2$  (Holloway *et al* 1968; Holloway

and Rees 1974). Since platinum is permeable to hydrogen at higher temperature and pressures, the released  $H_2$  escapes through the walls of platinum ampule. Silver oxalate decomposes at  $150^\circ C$  as:  $Ag_2C_2O_4 = 2Ag + 2CO_2$ . When low  $X_{CO_2}$  is desired, more water is added to the ampule.

About 100 mg of ignited  $Nd_2O_3$  (A-type), together with the above fluid-producing compounds are sealed in platinum ampules, using oxy-hydrogen microtorch. Precautionary cooling is done during welding to avoid any loss of the fluid during welding. This is also checked by weighing the ampule before and after welding. Extended heating at  $100^\circ C$  ensured the absence of any leak.

Experiments have been conducted with Tempress HR-1B-4 hydrothermal unit (Carborundum, Penn. State, USA), with stellite Tuttle-type reactor vessels (10 ml) at 1500 atm. and temperature  $200^\circ$ – $900^\circ C$ . All the runs were conducted for 50–60 hr which has been fixed experimentally as appropriate duration for equilibration. The reactor is quenched after each run, by blowing compressed air, until the temperature dropped down to about  $200^\circ C$ . It is further cooled to room temperature by dipping in cold water. The product is washed with distilled water and oven dried.

X-ray powder patterns are taken with  $CoK_\alpha$  radiation using Carl-Zeiss Debye-Scherrer Camera (114.6 mm). Infrared spectra are taken with CZ Jena UR-10 spectrometer in the range of  $400$ – $4000\text{ cm}^{-1}$ . Water and  $CO_2$  are determined by gas effluent method semimicrogravimetrically.

### 3. Results and discussion

The hydrothermal study of  $Nd_2O_3$ - $H_2O$ - $CO_2$  system at 1500 atm showed four stable phases:  $Nd(OH)_3$ -hexagonal,  $Nd(OH)CO_3$ -hexagonal,  $Nd_2O_2CO_3$ -hexagonal and  $NdOOH$ -monoclinic. The phase diagram is given in figure 1. There are two triple points. The first one is around  $780^\circ C$ , where  $Nd(OH)_3$ ,  $Nd_2O_2CO_3$  II and  $NdOOH$

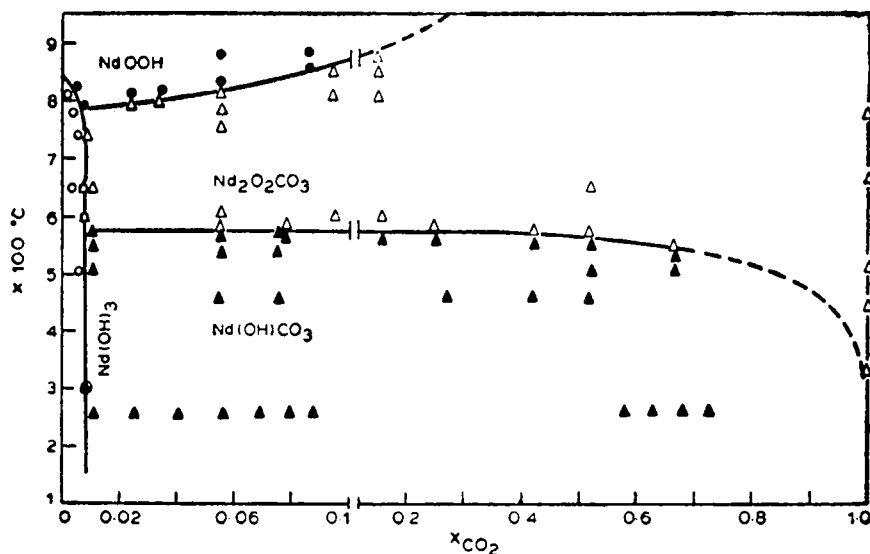


Figure 1.  $T$ - $X_{CO_2}$  topological plane for  $Nd_2O_3$ - $H_2O$ - $CO_2$  system at 1500 atm. The stable phases are marked by separate symbols.

are in equilibrium. The second triple point is around 575°C, where Nd(OH)<sub>3</sub>, Nd(OH)CO<sub>3</sub> and Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II coexist. Nd<sub>2</sub>O<sub>3</sub> field could not be identified even at the highest temperature of the present experimental work (900°C). Nd(OH)<sub>3</sub> field extends throughout the temperature range, from the ambient to 840°C, provided X<sub>CO<sub>2</sub></sub> is less than 0.008. The limiting boundaries of Nd(OH)<sub>3</sub> phase runs parallel to the temperature axis, while the boundaries of the other phases are perpendicular to the temperature axis. Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II field gradually widens with increasing CO<sub>2</sub> and eventually Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II is the only stable phase at X<sub>CO<sub>2</sub></sub> = 1.0 over the entire temperature range.

Certain apparently anomalous results of the previous workers (Shaffer and Roy 1959; Christensen 1973) can be explained in the light of the present work. The stability of Nd(OH)<sub>3</sub> up to 675°C, reported by Christensen is justifiable, provided X<sub>CO<sub>2</sub></sub> is extremely low. It can coexist with Nd(OH)CO<sub>3</sub>, Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and NdOOH, depending on the temperature range. This also explains the reports of Shaffer and Roy (1959), where the trihydroxide is said to be stable with NdOOH and Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II (the so called dense Nd(OH)<sub>3</sub> phase of Shaffer and Roy). According to Dexpert *et al* (1972) and Dexpert (1976), NdOOH is produced in the Nd<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system only when CO<sub>2</sub> is present as a catalysing impurity. This conclusion seems to be not valid for hydrothermal conditions, where NdOOH is a stable phase, directly in equilibrium with Nd(OH)<sub>3</sub>.

The important chemical equilibria involved in this phase diagram can be represented by the following reactions:

- (1)  $\text{Nd(OH)}_3 + \text{CO}_2 = \text{Nd(OH)CO}_3 + \text{H}_2\text{O}$
- (2)  $2 \text{Nd(OH)}_3 + \text{CO}_2 = \text{Nd}_2\text{O}_2\text{CO}_3 + 3 \text{H}_2\text{O}$
- (3)  $\text{Nd(OH)}_3 = \text{NdOOH} + \text{H}_2\text{O}$
- (4)  $\text{Nd(OH)CO}_3 = 0.5 \text{Nd}_2\text{O}_2\text{CO}_3 + 0.5 \text{CO}_2 + 0.5 \text{H}_2\text{O}$
- (5)  $\text{Nd}_2\text{O}_2\text{CO}_3 + \text{H}_2\text{O} = 2 \text{NdOOH} + \text{CO}_2$
- (6)  $\text{NdOOH} = 0.5 \text{Nd}_2\text{O}_3 + 0.5 \text{H}_2\text{O}$

Of these reactions, the formation of Nd<sub>2</sub>O<sub>3</sub> is beyond the temperature limit of the present investigation.

Two more triple points were anticipated in this system. The first one at low temperature region, with Nd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O, Nd(OH)CO<sub>3</sub> and Nd(OH)<sub>3</sub> in equilibrium and the other at higher temperature where NdOOH, Nd<sub>2</sub>O<sub>3</sub> and Nd(OH)<sub>3</sub> could be in equilibrium. However, within the experimental limits, these points could not be recognised. Only Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II is found to be stable, while the type I and IA, presumably stable at one atmosphere (Turcotte *et al* 1969), could not be stabilised. The x-ray data for Nd(OH)<sub>3</sub>, Nd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> II and Nd(OH)CO<sub>3</sub> are comparable with the reported values (table 1).

The infrared spectra of the different stable phases are given in figure 2. Nd(OH)<sub>3</sub> has only two absorption bands around 3610 cm<sup>-1</sup>, corresponding to O-H stretching

Table 1. X-ray patterns of the different phases obtained from hydrothermal studies.

Nd(OH) <sub>2</sub>				Nd(OH)CO <sub>3</sub> -B				Nd <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> -II			
dÅ	I	hkl	dÅ	I	hkl	dÅ	I	hkl	dÅ	I	hkl
5.539	S	100	5.851	S	100	4.945	M	002	7.816	M	002
3.223	S	110	4.010	MS	001	3.913	VW	120(?)	3.942	M	004
3.111	S	101	3.197	S	110	3.557	S	300	3.438	VVW	100
2.775	MS	200	2.969	S	200	3.185	MW	103	3.341	M	101
2.467	VWd	111	2.863	M	201	2.900	VS	302	3.145	W	005
2.245	VS	201	2.771	M	011	2.478	W	004	2.874	S	103
2.112	MS	120	2.337	M	210	2.280	VVW	?	2.632	MS	006
2.061	W	?	2.294	M	211	2.242	W	204	2.189	VVW	007(?)
2.034	W	?	1.972	S	300	2.112	VW	501	2.094	M	106
1.866	MS	300	1.910	M	020	2.060	MS	330	1.980	MS	111
1.838	S	211	1.856	VS	112	2.939	S	304	1.887	VS	107
1.779	VW	102	1.827	M	120	1.902	MS	332	1.777	M	114
1.619	MSd	220	1.804	W	311	1.787	M	600	1.636	MW	103
1.552	Wd	310	1.792	W	021(?)	1.741	VVW	305	1.588	M	116
1.433	Wd	311	1.727	VW	012, 121	1.678	M	602	1.568	MW	00.10
1.401	VW	212	1.624	W	?	1.586	M	206	1.432	M	10.10
1.325	MS	302	1.603	W	220	1.503	MW	306	1.370	M	207
1.311	VW	401	1.588	MS	301	1.447	MW	604	1.299	VVW	121
						1.350	MW	630	1.266	MW	123
						1.302	MS	632	1.239	W	124

Space group P 6 <sub>3</sub> /m	Space group P 2 <sub>1</sub> /m	Space group P 6 <sub>3c</sub> or P 6	Space group P 6 <sub>3</sub> /mmc
a = 6.450 Å	a = 6.235 Å	a = 12.383 Å	a = 3.988 Å
c = 3.761 Å	b = 3.830 Å	c = 9.962 Å	c = 15.69 Å
Z = 2	c = 4.242 Å	Z = 6	Z = 2
	β = 108.1°		
	Z = 2		

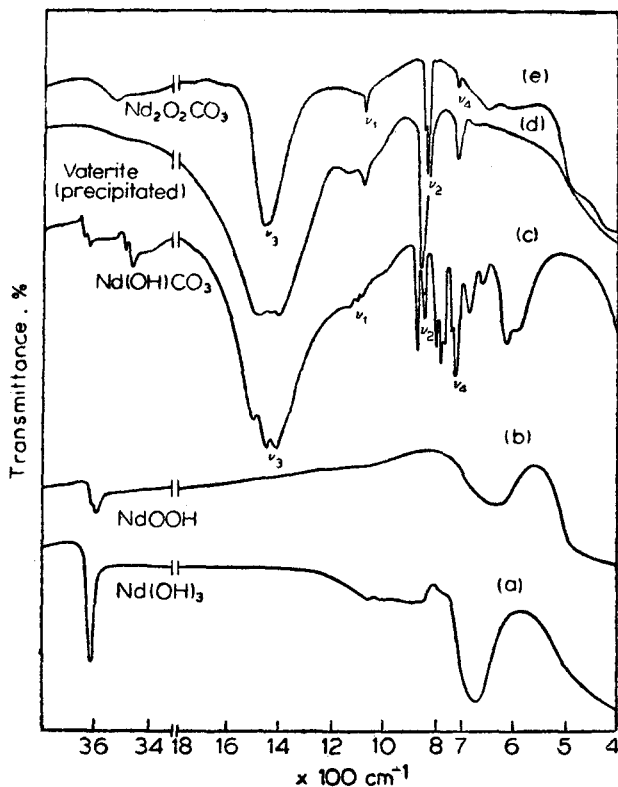


Figure 2. Infrared spectra of different phases obtained from hydrothermal investigations. The spectrum of precipitated vaterite is also given for comparison.

and another around  $673\text{ cm}^{-1}$  corresponding to OH librational mode. The OH groups have predominantly ionic character, in accordance with the  $\text{UCl}_3$ -type structure for  $\text{Nd}(\text{OH})_3$ . The  $\text{NdOOH}$  has broader and shallower bands in the  $3600\text{ cm}^{-1}$  region, corresponding to O-H stretching. The OH librational mode appears around  $626\text{ cm}^{-1}$ . Additional bands in the  $1000\text{--}1100\text{ cm}^{-1}$  may be observed in  $\text{CO}_2$  contaminated  $\text{NdOOH}$  samples.

For  $\text{Nd}(\text{OH})\text{CO}_3$ , there are two doublets in the O-H stretching region and the corresponding doublets in the librational modes appear in the  $600\text{--}700\text{ cm}^{-1}$  region. The intensity and the extent of separation of these bands are not identical. The multiplicity in the OH absorption bands suggests that they are nonequivalent and that a set of hydroxyl groups are hydrogen bonded to carbonate ions. Comparing with the stretching frequency of the hydroxides, those around  $3615$  and  $3635\text{ cm}^{-1}$  correspond to nonhydrogen bonded OH groups, while the absorptions around  $3470$  and  $3500\text{ cm}^{-1}$  arise from hydrogen bonded OH groups.

The absorption bands due to  $\text{CO}_3^{2-}$  groups in  $\text{Nd}(\text{OH})\text{CO}_3$  and  $\text{Nd}_2\text{O}_2\text{CO}_3$  can be compared with those of vaterite form of  $\text{CaCO}_3$ , with the site symmetry of  $\text{C}_{2v}$  instead of  $\text{D}_{3h}$ . The degeneracy of  $\nu_3$  and  $\nu_4$  bands are expected to be removed, but the splitting need not always be complete (Addler and Kerr 1963). In the case of vaterite,  $\nu_3$  band is split to three components, whereas  $\nu_4$  band remains unsplit. The carbonate bands of  $\text{Nd}_2\text{O}_2\text{CO}_3$  II compare well with those of vaterite. However,

splitting in  $\nu_2$  band is characteristic for the former. This splitting becomes more complex in the case of  $\text{Nd}(\text{OH})\text{CO}_3$  where the nondegenerate  $\nu_1$  band also is split to three absorptions of lower intensity. These splittings are explained in terms of non-equivalent  $\text{CO}_3^{2-}$  groups. Possibly, the site symmetry in  $\text{Nd}(\text{OH})\text{CO}_3$  for  $\text{CO}_3^{2-}$  is  $\text{C}_3$  with more restriction in the orientation of carbonate ion with respect to metal ions.

The band around  $800\text{ cm}^{-1}$  is tentatively assigned to M-O-H bending mode.

#### 4. Conclusions

(1)  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$  system is tremendously affected with small amount of  $\text{CO}_2$  ( $X_{\text{CO}_2} > 0.008$ ). (2)  $\text{Nd}(\text{OH})\text{CO}_3$  appears at very low  $X_{\text{CO}_2}$  values and is stable up to  $575^\circ\text{C}$  in low  $X_{\text{CO}_2}$  region. Its temperature of stability decreases with increasing  $X_{\text{CO}_2}$  values. (3)  $\text{Nd}(\text{OH})_3$  can coexist with all the other phases at low  $X_{\text{CO}_2}$ . (4)  $\text{Nd}(\text{OH})\text{CO}_3$ -hexagonal and  $\text{Nd}_2\text{O}_3\text{-CO}_3$ -hexagonal are the only stable carbonate phases under hydrothermal conditions.

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