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Hydrothermal Preparation of Rare Earth Hydroxycarbonates. The Crystal Structure of $NdOHCO_3$

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The rare earth hydroxycarbonates, $MeOHCO_3$, of La, Nd, and Sm, were prepared by using hydrothermal technique. The crystal structure of neodymium hydroxycarbonate, $NdOHCO_3$, was solved using three dimensional Patterson and Fourier functions and was refined to a conventional R-value of 8.2 %. The space group is $P\bar{6}$ with $a = 12.32$ Å and $c = 9.88$ Å. The unit cell contains 18 formula units. The neodymium atom is nine fold coordinated with oxygen atoms, and the structure has layers of $(NdOH^{2+})_n$ ions held together by the carbonate ions. The average distance for the bonds metal to oxygen (carbonate) is 2.52(1) Å, and for metal to oxygen (hydroxyl) is the average distance 2.45(2) Å. The intensities were measured on a three circle diffractometer with Weissenberg geometry. The powder patterns of $LaOHCO_3$ ($a = 12.616$ Å, $c = 10.022$ Å) and of $SmOHCO_3$ ($a = 12.231$ Å, $c = 9.856$ Å) are similar to that of $NdOHCO_3$ and it is assumed that the two compounds have the $NdOHCO_3$ structure.

In a hydrothermal investigation of the system $Nd_2O_3 - H_2O - CO_2$ over the temperature range 360 – 675°C and at pressures up to 3000 atm, three crystalline neodymium compounds were prepared hydrothermally.[1] Neodymium trihydroxide was obtained over the entire temperature-pressure range. At temperatures greater than 550°C the hexagonal modification of $Nd_2O_2CO_3$ was found,[2] and at temperatures below 530°C a previously unidentified phase (called Nd(I) in Ref. 1) was obtained. The crystal structure determination of this phase is reported below. It shows that the compound is $NdOHCO_3$.

Hydrothermal preparation of the compound $PrOHCO_3 \cdot 0.1H_2O$ was reported by Caro *et al.*[3] The compound was obtained by using hydrolysis of praseodymium carbonate at 250°C and 400 bar. Haschke and Eyring [4] obtained the compound $PrOHCO_3$ hydrothermally at 500°C, and the compound was also obtained up to 800°C. Weissenberg data indicated that praseodymium hydroxycarbonate was hexagonal with a structure analogous to bastnaesite,[5] and it was further concluded by Haschke and Eyring that a previously reported high-pressure form of lanthanum trihydroxide [6] actually was the hexagonal form of lanthanum hydroxycarbonate. The unit cells of the mentioned rare earth hydroxycarbonates are listed in Table 1.

Table 1. Unit cell parameters of some rare earth hydroxycarbonates.

	a Å	*c* Å
$LaOHCO_3$, Ref. 6. (reported as high pressure $La(OH)_3$)	4.214	5.041
$CeFCO_3$, Bastnaesite, Ref. 5.	7.162	9.787
$PrOHCO_3.0.1\ H_2O$, Ref. 3.	7.152	9.862
$PrOHCO_3$, Ref. 4.	4.146	4.986

EXPERIMENTAL

Rare earth carbonates were precipitated with a 1 M $KHCO_3$ solution from dilute solutions of rare earth nitrates prepared by dissolving the oxides in nitric acid. The freshly precipitated carbonates were washed with water and treated with water saturated with carbon dioxide or with a 0.3 M $KHCO_3$ solution in pressure vessels lined with pure silver or pure gold at the experimental conditions listed in Table 2. The products were washed

Table 2. Experimental conditions for hydrothermal preparation of rare earth hydroxy carbonates.

Exp. No.	Initial conditions: Freshly precipitated	Liner of vessel	Temp °C	Pressure atm	Time h	Solvent	Product
1.	Lanthanum carbonate	Ag	300	75	48	0.3 M $KHCO_3$	$LaOHCO_3$ pure
2.	Neodymium hydroxide	Au	420	1800	44	H_2O+CO_2[a]	$NdOHCO_3+Nd(OH)_3$
3.	Samarium carbonate	Ag	300	75	48	0.3 M $KHCO_3$	$SmOHCO_3$ pure

[a] Water saturated with carbon dioxide.

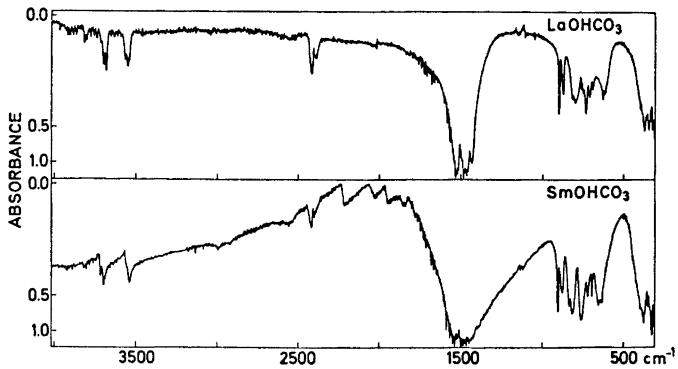

Fig. 1. Infra-red spectra of $LaOHCO_3$ and $SmOHCO_3$.

Table 3. X-Ray powder patterns of some rare earth hydroxycarbonates.

$LaOHCO_3$, a = 12.616(8) Å, c = 10.022(5) Å.

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	5.032	5.011	61
3	0	0	3.649	3.642	82
3	0	2	2.949	2.946	100
0	0	4	2.503	2.506	22
3	3	0	2.103	2.103	49
3	0	4	2.063	2.064	69
3	3	2	1.938	1.939	45
6	0	0	1.820	1.821	22
6	0	2	1.710	1.712	27
3	3	4	1.610	1.611	25
3	0	6	1.517	1.518	21
6	0	4	1.473	1.473	19
6	3	0	1.377	1.377	19
6	3	2	1.328	1.327	16
3	3	6	1.309	1.308	23

$NdOHCO_3$, a = 12.34(1) Å, c = 9.915(6) Å.

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	4.964	4.958	58
3	0	0	3.569	3.563	74
3	0	2	2.899	2.893	100
0	0	4	2.485	2.479	17
3	3	0	2.061	2.057	50
3	0	4	2.039	2.035	68
3	3	2	1.903	1.900	43
6	0	0	1.783	1.782	11
6	0	2	1.679	1.677	24
3	3	4	1.586	1.583	22
3	0	6	1.501	1.499	19
6	0	4	1.447	1.447	10
6	3	0	1.347	1.347	13
6	3	2	1.301	1.300	19
3	3	6	1.288	1.288	26

$SmOHCO_3$, a = 12.231(8) Å, c = 9.856(4) Å.

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	4.950	4.928	67
3	0	0	3.539	3.531	63
3	0	2	2.875	2.870	100
0	0	4	2.466	2.464	28
3	3	0	2.039	2.039	30
3	0	4	2.019	2.021	67
3	3	2	1.884	1.884	47
6	0	0	1.765	1.765	22
6	0	2	1.662	1.662	24
0	0	6	1.643	1.643	5
3	3	4	1.570	1.571	28
3	0	6	1.489	1.489	25
6	0	4	1.435	1.435	16
6	3	0	1.333	1.335	14
6	3	2	1.289	1.288	21
3	3	6	1.279	1.279	9

with water and dried in air at room temperature. Chemical analyses were made on samples that only contained one phase using EDTA titrations.[7] (Found: La 64.03. Calc. for $LaOHCO_3$: La 64.34. Found: Sm 66.14. Calc. for $SmOHCO_3$: Sm 66.13).

The IR spectra of the pure compounds were recorded over the frequency range 4000 to 400 cm^{-1} with a Perkin-Elmer 521 spectrophotometer using pellets of mixtures of 2 mg of sample and 200 mg of CsI. The spectra are recorded in Fig. 1.

X-Ray powder patterns were obtained with a Guinier camera using Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) with NaCl ($a = 5.6389$ Å) or Ge ($a = 5.6576$ Å) as internal standards. The intensities of the powder lines were measured using a Joyce double beam recording microdensitometer. The powder patterns are listed in Table 3.

A single crystal of $NdOHCO_3$ with the dimensions $0.1 \times 0.1 \times 0.35$ mm^3 was investigated using film technique. Weissenberg photographs were taken of *hk*0, *hk*1, and *hk*2, and precession photographs were taken of *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l*, and 0*kl*. No systematic absences were found. A total of 1145 independent *hkl* reflections with $I > 3\ \sigma(I)$ were measured on a single crystal diffractometer with a scintillation counter using monochromatic Ag$K\alpha$-radiation ($\lambda = 0.5608$ Å) in conjunction with a pulse height analyzer. The diffractometer was a three circle diffractometer with Weissenberg geometry, using a ϕ-scan in the integration of the intensities. The monochromator was a graphite crystal. Lorentz-polarization corrections were applied and absorption corrections were made using Wells' method.[8]

STRUCTURE DETERMINATION

Several hexagonal space groups have no limiting conditions for the possible reflections. Attempts were made to refine the structure using all these possible hexagonal space groups. It was only possible to refine the structure using the space group $P\bar{6}$ (No. 174). A three-dimensional Patterson function showed strong maxima at the positions ($p/3$, $q/3$, $r/2$), where p and q have the values 0, 1, 2 and r the values 0 and 1. All these maxima had approximately the same heights and were interpreted as Nd-Nd-vectors. Of the observed *hkl* reflections strong intensities were only present when the conditions $h = 3n$, $k = 3n$, and $l = 2n$ was satisfied for the reflections. This indicates a layer structure with

neodymium atoms placed in layers parallel to the *ab*-plane, with Nd–Nd distances close to $a/3$ within the layers and with distances between the layers in the *c*-direction close to $c/2$. The weak *hkl* reflections may have scattering contributions from the metal atoms, if the metal-metal distances deviate from the distances $a/3$ and $c/2$, and will in all cases have scattering contributions from the light atoms in the structure.

From packing considerations where some of the oxygen atoms were placed in the special positions 2*i*, 2*h*, and 2*g* of the space group with *z* coordinates close to $\pm 1/4$, it was found that a model with neodymium atoms in the general position 6*l* at (0.22,0.12,0.25), (0.22,0.44,0.25), and (0.55,0.12,0.25) would give acceptable neodymium oxygen distances and would be in agreement with the calculated three-dimensional Patterson function. A combination of packing considerations and three-dimensional Fourier maps phased on this model gave after a series of refinement cycles and Fourier calculations the positions of all the oxygen and carbon atoms of the carbonate groups and the oxygen atoms of the hydroxyl groups. The refinements applied the methods of least squares and isotropic temperature factors. The program used was the Fortran crystallographic least squares program LINUS.[9] The refinement proceeded only to a conventional *R*-value of 17.5 %. The occupancy of two of the neodymium atoms was introduced as parameters and after a series of refinement cycles using isotropic temperature factors for all the atoms an *R*-value of 12.2 % was obtained. The oxygen and carbon atoms belonging to the carbonate ions had at this stage obtained positions corresponding to distorted and not planar carbonate ions. Further refinements proceeded with a least squares program (Pawley [10]) using constrained refinement of the atoms belonging to the carbonate ions and using anisotropic temperature factors for the metal atoms. The refinement proceeded to a conventional *R*-value of 8.2 %. No attempts were made to determine the position of the hydrogen atoms belonging to the hydroxyl ions. It was not possible to refine the structure in hexagonal space groups with higher symmetry than that of $P\bar{6}$.

CRYSTAL DATA

The unit cell of the compound $NdOHCO_3$ contains 18 formula units. The crystal system is hexagonal with the space group $P\bar{6}$ (No. 174). The axes determined from the diffractometer setting are $a = 12.32$ Å, $c = 9.88$ Å. The calculated density is 5.09 g/cm^3, and the absorption coefficient for Ag-radiation is 93 cm^{-1}. The structure factors for the atoms were calculated from the atomic scattering factors reported by Cromer and Mann.[11] Atomic coordinates and temperature factor parameters are listed in Table 4, interatomic distances and bond angles are in Table 5, and observed and calculated structure factors are listed in Table 6. Fig. 2 shows the positions of the atoms listed in Table 4 and the positions of the pertinent symmetry related atoms to form the metal oxygen coordination polyhedra of the three neodymium atoms.

Table 4. Atomic coordinates and temperature factors with standard deviations of $NdOHCO_3$. Diffractometer data, $R = 8.2$ %.

Atom	x	y	z	B (Å^2)
O_1	0.511(2)	0.755(2)	0.0	1.0(2)
C_1	0.510(3)	0.648(3)	0.0	1.7(4)
O_2	0.512(1)	0.596(1)	0.115(1)	1.0(3)
O_3	−0.101(3)	0.090(3)	0.0	3.0(5)
C_2	0.014(4)	0.185(4)	0.0	3.0(6)
O_4	0.073(1)	0.231(1)	0.115(1)	2.3(2)
O_5	0.529(4)	0.095(3)	0.0	3.0(6)
C_3	0.460(4)	0.149(4)	0.0	3.0(6)
O_6	0.428(1)	0.178(1)	0.115(1)	1.7(2)
O_7	0.501(1)	0.703(1)	0.5	0.2(2)
C_4	0.444(3)	0.580(3)	0.5	1.9(4)
O_8	0.419(1)	0.519(1)	0.615(1)	1.3(2)
O_9	0.572(3)	0.433(3)	0.5	3.0(5)
C_5	0.470(5)	0.322(5)	0.5	5.1(9)
O_{10}	0.422(1)	0.265(1)	0.615(1)	2.3(2)
O_{11}	0.183(2)	0.096(2)	0.5	2.3(4)
C_6	0.171(3)	0.196(3)	0.5	2.5(5)
O_{12}	0.169(2)	0.248(1)	0.615(1)	2.9(3)
O_{13}	0.0	0.0	0.272(2)	1.4(3)
O_{14}	1/3	2/3	0.230(2)	1.5(3)
O_{15}	2/3	1/3	0.230(3)	3.3(5)
O_{16}	0.339(1)	0.019(1)	0.321(1)	1.7(2)
O_{17}	0.654(2)	−0.012(2)	0.180(2)	3.0(3)
Nd_1	0.2284(1)	0.1226(1)	0.2375(1)	0.95(2)[a]
Nd_2	0.2092(2)	0.4363(1)	0.2638(2)	0.83(2)[a]
Nd_3	0.5515(3)	0.1060(1)	0.2537(3)	1.00[a]

Anisotropic temperature factor parameters of the neodymium atoms with standard deviations ($\times 10^5$).

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Nd_1	999	48	828	56	1400	46	770	41	259	39	−4	34
Nd_2	163	53	432	44	810	47	−104	35	760	31	348	38
Nd_3	2026	66	1137	53	2242	54	613	37	−353	52	456	51

[a] The values listed are the occupancy factor of the metal atoms.

DISCUSSION

The investigation shows that the hydroxycarbonates of lanthanum, neodymium, and samarium can be prepared by hydrothermal technique. The powder patterns of the three compounds are similar to each other, and it is assumed that the compounds all belong to the same hexagonal structure described above. In the powder patterns reflections are only observed with indices that satisfy the condition $h = 3n$, $k = 3n$, and $l = 2n$ (see Table 3). The

Table 5. Interatomic distances (Å) and bond angles (degrees). Standard deviations in parentheses.

Nd_1-O_3'	2.38	(1)	$O_{11}-Nd_1-O_{12}'$	52.5	(9)
Nd_1-O_4'	2.43	(2)	$O_{11}-Nd_1-O_{10}'$	66.3	(6)
Nd_1-O_6	2.51	(2)	$O_{11}-Nd_1-O_{16}$	75.0	(8)
Nd_1-O_{10}'	2.59	(1)	$O_{11}-Nd_1-O_{13}$	71.4	(7)
Nd_1-O_{11}	2.64	(1)	$O_3'-Nd_1-O_{17}'$	82.0	(8)
Nd_1-O_{12}'	2.49	(1)	$O_3'-Nd_1-O_6$	70.4	(9)
Nd_1-O_{13}	2.46	(1)	$O_3'-Nd_1-O_4'$	56.4	(9)
Nd_1-O_{16}	2.43	(2)	$O_{13}-Nd_1-O_{17}'$	121.5	(6)
Nd_1-O_{17}'	2.46	(2)	$O_{17}'-Nd_1-O_{16}$	123.2	(6)
			$O_{16}-Nd_1-O_{13}$	113.6	(3)
Nd_2-O_1'	2.67	(1)	$O_7'-Nd_2-O_{12}'$	79.0	(6)
Nd_2-O_2'	2.44	(1)	$O_7'-Nd_2-O_{16}'$	75.9	(4)
Nd_2-O_4	2.67	(1)	$O_7'-Nd_2-O_8'$	67.9	(5)
Nd_2-O_7'	2.47	(1)	$O_1'-Nd_2-O_4$	69.1	(5)
Nd_2-O_8'	2.55	(1)	$O_1'-Nd_2-O_2'$	52.7	(6)
Nd_2-O_{12}'	2.43	(2)	$O_1'-Nd_2-O_{14}$	69.9	(6)
Nd_2-O_{14}	2.48	(1)	$O_1'-Nd_2-O_{17}'$	73.6	(7)
Nd_2-O_{16}'	2.50	(1)	$O_{16}'-Nd_2-O_{14}$	123.9	(4)
Nd_2-O_{17}'	2.45	(3)	$O_{14}-Nd_2-O_{17}'$	107.7	(4)
			$O_{17}'-Nd_2-O_{16}'$	126.8	(5)
Nd_3-O_2''	2.53	(1)	$O_9'-Nd_3-O_{10}''$	55.8	(9)
Nd_3-O_5	2.52	(1)	$O_9'-Nd_3-O_8''$	67.9	(8)
Nd_3-O_6	2.52	(2)	$O_9'-Nd_3-O_{16}$	76.9	(8)
Nd_3-O_8''	2.58	(2)	$O_5-Nd_3-O_6$	53.7	(9)
Nd_3-O_9'	2.46	(1)	$O_5-Nd_3-O_{15}$	87.0	(9)
Nd_3-O_{10}''	2.40	(2)	$O_5-Nd_3-O_{17}$	75.4	(9)
Nd_3-O_{15}	2.44	(1)	$O_5-Nd_3-O_2''$	53.4	(7)
Nd_3-O_{16}	2.37	(2)	$O_{16}-Nd_3-O_{15}$	115.1	(5)
Nd_3-O_{17}	2.47	(3)	$O_{15}-Nd_3-O_{17}$	118.3	(5)
			$O_{17}-Nd_3-O_{16}$	126.1	(6)

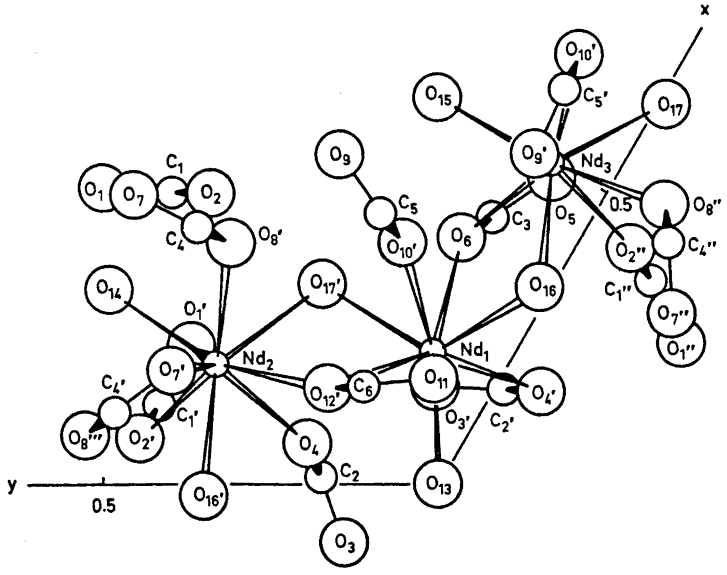

Fig. 2. Projection of the metal oxygen coordination polyhedra on (001).

Table 6. Observed and calculated structure factors of $NdOHCO_3$. Reading from the left to the right, the column contains the values h, k, l, F_{obs}, F_{calc}.

Table 6. Continued.

5	0	8	15	16	10	3	8	28	35	4	7	9	99	65	1	1	10	9	9	5	6	10	25	29	3	3	11	33	26	2	4	12	29	25
5	1	8	44	47	11	1	8	52	54	4	8	9	77	68	1	2	10	28	22	5	7	10	49	50	3	4	11	68	64	2	5	12	16	24
5	2	8	42	51	11	2	8	68	64	5	0	9	186	168	1	3	10	25	26	6	0	10	249	238	3	5	11	106	101	2	6	12	23	31
5	3	8	31	32	12	0	8	205	188	5	1	9	98	108	1	4	10	44	48	6	1	10	34	32	3	6	11	32	38	3	1	12	28	19
5	4	8	51	55	12	1	8	59	63	5	2	9	38	36	1	5	10	34	33	6	2	10	29	35	3	7	11	47	50	3	2	12	26	25
5	5	8	53	55	1	1	9	19	21	5	3	9	101	112	1	6	10	31	34	6	3	10	228	213	4	0	11	84	83	3	3	12	191	178
5	6	8	33	42	1	2	9	88	106	5	4	9	89	83	1	7	10	59	62	6	4	10	29	28	4	1	11	33	33	3	4	12	16	17
5	7	8	48	57	1	3	9	79	92	5	5	9	47	58	1	8	10	35	39	6	5	10	27	28	4	2	11	82	81	3	5	12	24	18
5	8	8	56	57	1	4	9	62	66	5	6	9	81	98	1	9	10	39	36	6	6	10	193	172	4	3	11	66	65	4	0	12	17	12
5	9	8	44	48	1	5	9	98	97	5	7	9	82	68	2	0	10	19	13	7	0	10	15	28	4	4	11	39	35	4	1	12	22	25
6	0	8	294	338	1	6	9	62	70	5	8	9	27	35	2	1	10	19	20	7	1	10	99	61	4	5	11	88	87	4	2	12	26	28
6	1	8	35	43	1	7	9	55	53	6	0	9	27	28	2	2	10	41	38	7	2	10	39	48	4	6	11	65	56	4	3	12	16	18
6	2	8	87	48	1	8	9	87	83	6	1	9	24	24	2	3	10	24	22	7	4	10	59	58	5	0	11	111	104	5	0	12	20	18
6	3	8	283	286	1	9	9	58	62	6	2	9	96	96	2	4	10	38	33	7	5	10	45	46	5	1	11	104	98	5	1	12	26	29
6	4	8	43	40	1	10	9	48	44	6	3	9	28	39	2	5	10	32	35	8	1	10	48	42	5	2	11	21	26	5	2	12	17	28
6	5	8	31	32	2	0	9	103	111	6	4	9	49	49	2	6	10	31	33	8	2	10	42	49	5	3	11	111	103	5	3	12	24	21
6	6	8	238	221	2	1	9	93	102	6	5	9	79	84	2	7	10	40	40	8	3	10	21	26	5	4	11	94	82	6	0	12	165	165
6	7	8	34	33	2	3	9	99	102	6	6	9	25	32	2	8	10	43	49	8	4	10	220	198	5	5	11	43	44	6	1	12	27	26
6	8	8	28	29	2	4	9	92	85	6	7	9	40	31	2	9	10	27	42	9	1	10	40	39	6	0	11	37	35	6	2	12	28	27
7	1	8	48	46	2	5	9	31	33	7	0	9	37	47	3	1	10	28	28	9	2	10	38	37	6	1	11	87	74	7	1	12	27	33
7	2	8	57	55	2	6	9	97	96	7	1	9	57	55	3	2	10	24	28	10	1	10	58	58	6	2	11	105	94	1	0	13	41	79
7	4	8	60	63	2	7	9	75	76	7	2	9	72	72	3	3	10	233	236	1	0	11	65	69	6	3	11	34	32	1	1	13	13	14
7	5	8	50	56	2	8	9	38	42	7	3	9	45	45	3	4	10	26	28	1	2	11	93	98	6	4	11	69	49	1	2	13	90	93
7	6	8	26	34	2	9	9	83	88	7	4	9	61	59	3	5	10	24	18	1	3	11	88	82	7	0	11	78	59	1	3	13	74	77
7	7	8	53	68	2	10	9	78	69	7	5	9	77	66	3	6	10	233	211	1	4	11	32	31	7	1	11	49	47	1	4	13	22	19
8	0	8	19	21	3	0	9	32	32	7	6	9	40	35	3	8	10	21	15	1	5	11	101	93	7	2	11	82	75	2	0	13	83	93
8	1	8	51	52	3	1	9	84	87	8	0	9	99	100	4	0	10	13	22	1	6	11	79	78	7	3	11	53	56	2	1	13	98	83
8	2	8	56	54	3	2	9	99	103	8	1	9	92	89	4	1	10	42	43	1	7	11	46	47	8	0	11	89	86	2	2	13	32	30
8	3	8	28	16	3	3	9	35	31	8	2	9	41	46	4	2	10	28	32	1	8	11	81	79	8	1	11	67	82	2	3	13	67	67
8	4	8	66	61	3	4	9	74	71	8	3	9	98	93	4	3	10	19	28	2	0	11	109	105	8	2	11	47	46	2	4	13	81	71
8	5	8	62	60	3	5	9	99	105	8	4	9	83	74	4	4	10	32	39	2	2	11	81	88	8	4	11	28	29	3	0	13	98	88
8	6	8	33	30	3	6	9	27	19	8	5	9	25	36	4	5	10	36	98	2	3	11	96	98	1	2	12	27	23	3	1	13	77	72
9	0	8	264	250	3	7	9	41	42	9	0	9	38	31	4	6	10	25	29	2	4	11	87	83	1	3	12	20	23	3	2	13	88	86
9	1	8	43	47	3	8	9	89	92	9	1	9	64	96	4	7	10	52	61	2	5	11	22	27	1	4	12	21	26	3	3	13	34	29
9	2	8	57	55	4	0	9	79	77	9	2	9	85	81	5	0	10	16	15	2	6	11	104	108	1	5	12	23	27	4	0	13	71	71
9	3	8	246	233	4	1	9	63	58	9	3	9	24	27	5	1	10	32	28	2	7	11	82	69	1	6	12	20	26	4	1	13	20	19
9	4	8	52	48	4	2	9	98	89	10	0	9	43	30	5	2	10	31	34	2	8	11	47	44	1	7	12	21	32	4	2	13	78	73
9	5	8	38	43	4	3	9	74	74	10	1	9	45	41	5	3	10	28	18	3	0	11	98	94	2	0	12	20	14					
10	1	8	56	59	4	5	9	83	80	10	2	9	63	65	5	4	10	49	47	3	1	11	82	86	2	1	12	26	18					
10	2	8	58	57	4	6	9	41	54	11	0	9	108	101	5	5	10	51	51	3	2	11	97	93	2	3	12	24	22					

powder patterns could thus be indexed on hexagonal cells with $a_H = a/3$, and $c_H = c/2$. Such cells would, however, only contain one formula unit of $MeOHCO_3$, which is in conflict with all the hexagonal space groups. From single crystal investigations of $NdOHCO_3$ the correct unit cell has been found, and it has been assumed that the correct unit cells of $LaOHCO_3$ and of $SmOHCO_3$ have the dimensions listed in Table 3. A plot of the unit cell parameters *vs.* the ionic radii [2] are shown in Fig. 3. which illustrates the lanthanide contraction.

Caused by the uneven scattering power of the heavy metal atom and the light oxygen and carbon atoms, it should not be expected that an X-ray investigation would give a structure with a high precision in the determination of the positions of the light atoms. Using the atomic numbers of the elements

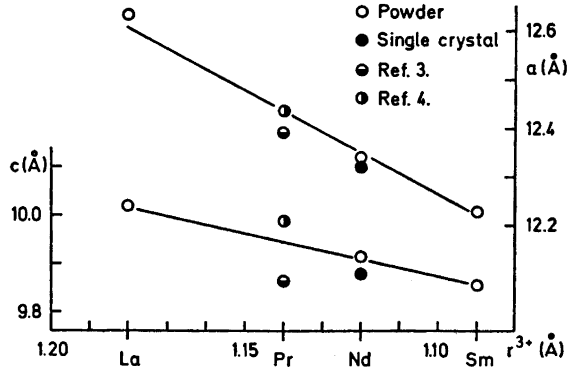

Fig. 3. Unit cell parameters (Å) of hexagonal rare earth hydroxycarbonates *vs.* ionic radii of Me^{3+} (Å). The unit cells from Refs. 3 and 4 are transformed to unit cells containing 18 formula units.

in $NdOHCO_3$ in a calculation of scattering contributions, it is found that the metal atom has an average scattering contribution of 92.5 % of the total intensity, and all the other atoms are only contributing with 7.5 % to the total intensity. In the last Fourier maps calculated, it was, however, possible to identify all the light atoms of the structure.

The occupancy factors of Nd_1 and Nd_2 have been used as parameters in the refinements and the occupancy factor of Nd_2 is significantly different from 1.0. Nd_2 is coordinated with the oxygen atoms of the carbonate ions in a way different from that of Nd_1 and Nd_3 (see Fig. 2). The carbonate ions $O_1'-C_1'-O_2'$ and $O_7'-C_4'-O_8'''$ are almost superimposed upon each other, and Nd_2 is bonded to the atoms O_1', O_2', and O_7'. The carbonate ions $O_3'-C_2'-O_4'$ and $O_{11}-C_6-O_{12}'$ are not superimposed upon each other, and Nd_1 is bonded to O_3', O_4', O_{11}, and O_{12}', and the carbonate ions $O_5-C_3-O_6$ and $O_9'-C_5'-O_{10}'$ are not superimposed upon each other, and Nd_3 is bonded to O_5, O_6, O_9', and O_{10}'. It is also observed (see below) that Nd_2 has the longest metal-oxygen distances. The coordination of Nd_2 is thus different from the coordination of Nd_1 and Nd_3. This can possibly explain that the number of vacancies at the position of Nd_2 is different from and greater than the number of vacancies at the positious of the atoms Nd_1 and Nd_3. No attempts have been made to introduce occupancy factors of the atoms to which Nd_2 is bonded as parameters in the refinements.

The three metal atoms are nine coordinated with oxygen atoms. Six oxygen atoms belong to carbonate ions and three oxygen atoms to hydroxyl ions. The average distances for the bonds metal to oxygen (carbonate) are Nd_1-O 2.51(1) Å, Nd_2-O 2.54(1) Å, and Nd_3-O 2.50(1) Å, and for metal to oxygen (hydroxyl) are the average distances Nd_1-O 2.45(2) Å, Nd_2-O 2.48(2) Å, and Nd_3-O 2.43(2) Å.

The neodymium-oxygen (carbonate) distances found in $NdOHCO_3$ are comparable with the corresponding distances of 2.47(3) Å and 2.64(2) Å found in $Nd_2O_2CO_3$.[2]

The crystal structure of $NdOHCO_3$ and that of $Nd_2O_2CO_3$ have common characteristics. Both structures are layer structures with the layers held together by the carbonate ions. Two of the three oxygen atoms of the carbonate ions are placed superimposed upon each other in the direction of the *c*-axis, and the third oxygen atom and the carbon atom are placed on mirror planes perpendicular to the *c*-axis. The carbonate ions are ordered in the $NdOHCO_3$ structure and are statistically arranged in the structure of $Nd_2O_2CO_3$. The carbon oxygen distances of 1.31(1) Å are in good agreement with distances of 1.28 Å found in the carbonate ions of $KHCO_3$ by neutron diffraction.[13]

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