ACTA CHEMICA SCANDINAVICA 24 (1970) 2440–2446

Hydrothermal Preparation of Neodymium Oxide Carbonate

The Location of the Carbonate Ion in the Structure of $Nd_2O_2CO_3$

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The neodymium oxide carbonate, $Nd_2O_2CO_3$, was prepared from freshly precipitated neodymium hydroxide and an aqueous solution of carbon dioxide, using the hydrothermal technique. The crystal structure was investigated using Patterson and Fourier functions and was refined to a conventional R value of 5.0 %. The space group is $P6_3/mmc$ with $a = 3.974$ Å and $c = 15.703$ Å. The neodymium atom is eight fold coordinated with oxygen atoms, and the coordination polyhedron is a rhombohedron. The carbonate ion has the symmetry C_{2v}.

The existence of three polymorphic crystalline forms of $Ln_2O_2CO_3$, rare earth oxide carbonate, was reported by Sawyer, Caro and Eyring.[1] All three forms are layer structures containing $(Ln_2O_2^{2+})_n$ polymers and CO_3^{2-}-ions. Type I has a square $(Ln_2O_2^{2+})_n$ layer; Type II has a hexagonal $(Ln_2O_2^{2+})_n$ layer,[2] also found in the A-form of Ln_2O_3. The third modification called type IA of $Nd_2O_2CO_3$ is obtained by heating type I $Nd_2O_2CO_3$ in air at 420 – 500°C, and type II $Nd_2O_2CO_3$ is obtained from type I $Nd_2O_2CO_3$ by heating to 710°C.[2] The type I $Nd_2O_2CO_3$ is obtained by decomposition of the corresponding oxalate in air at 420°C, and type II $Nd_2O_2CO_3$ is obtained by decomposition of the oxalate in a stream of carbon dioxide at 500 – 600°C.[1]

From the Debye-Scherrer powder pattern the space group $P6_3/m$ was deduced for type II $Nd_2O_2CO_3$ with $a = 3.991$ Å and $c = 15.66$ Å. From packing considerations a structure related to that of the A-form of Ln_2O_3 was suggested.[1] A projection of a part of the structure in the [100] direction is given on Fig. 1. The carbonate group has a carbon atom at $(x,2x,\frac{1}{4})$, and oxygen atoms at $(x',2x',\frac{1}{4})$ and $(0,0,z)$.[1] The infra-red spectrum of type II $Nd_2O_2CO_3$ is in agreement with this structure model, indicating a C_{2v} symmetry of the carbonate ion.[2]

In order to determine the position of the carbonate ion in the structure of type II $Nd_2O_2CO_3$ it was decided to grow single crystals of the compound using hydrothermal preparations, and to do a three dimensional single crystal X-ray analysis of the structure.

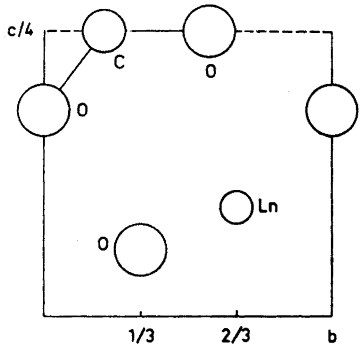

Fig. 1. Projection in the [100] direction of a part of the structure of $Ln_2O_2CO_3$ (type II). This solution of the structure was obtained from packing considerations.[1]

EXPERIMENTAL

Chemistry. In a typical hydrothermal experiment 0.1 g of freshly precipitated neodymium hydroxide was sealed with 0.7 ml of water saturated with carbon dioxide in a 2 ml gold ampoule. The ampoule was placed in a 7 ml pressure vessel and was heated to 665°C at a pressure of 2040 atm for 27 h. The main part of the product was flat crystals shaped as regular hexagons (type II $Nd_2O_2CO_3$) and a minor part of the product was small needles ($Nd(OH)_3$). The product was washed with water and dried in air at room temperature.

Physical measurement. The infra-red spectrum was recorded over the frequency range 600 – 1800 cm^{-1} on a Beckman IR 10 spectrophotometer using a pellet of a mixture of 3 mg sample in 200 mg of CsI. The spectrum is given in Fig. 2.

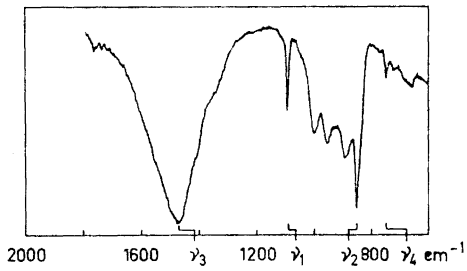

Fig. 2. Infra-red spectrum of $Nd_2O_2CO_3$. The shift in the frequencies for the four modes of the free carbonate ion from $\nu_1=1063$ cm^{-1}, $\nu_2=879$ cm^{-1}, $\nu_3=1415$ cm^{-1}, $\nu_4=680$ cm^{-1} (Ref. 2) to the values, $\nu_1=1090$ cm^{-1}, $\nu_2=850$ cm^{-1}, $\nu_3=1470$ cm^{-1} and $\nu_4=750$ cm^{-1}, is indicated. The ν_1 mode is inactive for the free ion but is present in this compound, indicating a dipole within the carbonate ion. The symmetry of the carbonate ion is C_{2v} or C_s. The structure investigation proved it to have the symmetry C_{2v}.

X-Ray technique. The powder pattern of $Nd_2O_2CO_3$ was obtained with a Guinier-de Wolff camera using Cu$K\alpha$ radiation ($\lambda=1.5418$ Å), and germanium as an internal standard ($a_{Ge}=5.6576$ Å). The pattern given in Table 1 was indexed using a hexagonal unit cell with $a=3.974$ Å and $c=15.703$ Å.

A flat single crystal shaped as a regular hexagon with an edge length of 0.0053 cm, and with a thickness of 0.0006 cm was investigated using precession methods. Photographs were taken with Zr-filtered Mo$K\alpha$ radiation of (0*kl*), (*hk*0), (*hk*1), (*hk*2), and (*hk*3). A total of 124 independent *hkl* reflection with $I > 2\sigma(I)$ were measured with a diffractometer of the Arndt-Phillips design using Mo$K\alpha$ radiation monochromated by reflection from a graphite crystal and using a scintillation counter in conjunction with a pulse heigt analyzer. Lorentz-polarisation corrections were applied (program G404) [3] and absorption corrections were made using Well's method.[4]

Table 1. X-Ray powder pattern of $Nd_2O_2CO_3$. $a=3.974$ Å, $c=15.703$ Å. The intensities are estimated visually.

$h\,k\,l$	d_{obs}(Å)	d_{calc}(Å)	I_{obs}
0 1 0	3.451	3.442	m
0 1 1	3.369	3.362	vs
0 1 2	3.163	3.152	m
0 1 3	2.885	2.876	s
0 0 6	2.620	2.617	w
0 1 4	2.594	2.588	w
0 1 6	2.084	2.083	w
1 1 0	1.990	1.987	s
1 1 2	1.930	1.926	w
0 1 7	1.881	1.879	w
1 1 4	1.773	1.773	m
0 2 0	1.723	1.721	w
0 2 1	1.714	1.711	m
0 2 2	1.682	1.681	vw
0 2 3	1.637	1.635	w
1 1 6	1.582	1.583	w
0 2 4	1.578	1.576	vw
0 0 10	1.570	1.570	w
0 1 10	1.429	1.429	w
0 2 7	1.366	1.365	w
1 2 1	1.299	1.296	m
1 2 3	1.263	1.262	m

vs: very strong s: strong m: medium w: weak vw: very weak

STRUCTURE DETERMINATION

The symmetry of the precession photographs is in agreement with the space group $P6_3/mmc$ (No. 194). A Patterson projection in the [100] direction gave the position of a neodymium atom at $(0,\frac{2}{3},0.095)$. A Fourier projection in the [100] direction (Fig. 3) phased on this assumption gave the positions of oxygen atoms at (0,0,0.18), $(0,\frac{2}{3},0.555)$, and $(0,0.57,\frac{1}{4})$. The positions $(\frac{1}{3},\frac{2}{3},0.095)$ for neodymium, $(\frac{1}{3},\frac{2}{3},0.555)$ and (0,0,0.18) for oxygen atoms are in agreement with the structure reported in Ref. 1. The peak at (0, 0, 0.18) represents two of the oxygen atoms in the carbonate ion. The third oxygen atom is in the position $(0.285,0.57,\frac{1}{4})$, and the position of the carbon atom will then be $(0.10,0.20,\frac{1}{4})$. As the position $(x,2x,\frac{1}{4})$ has a multiplicity of six, the third oxygen atom and the carbon atom are assumed to be statistically distributed with $\frac{1}{3}$ atom in the position $(x,2x,\frac{1}{4})$. The refinement proceeded by the methods of least squares (G403)[5] using isotropic temperature factors giving an R-value of 5.0 % at the end of the refinement.

CRYSTAL DATA

The compound $Nd_2O_2CO_3$ has two formula units in the unit cell. The crystal system is hexagonal with $a=3.974$ Å, $c=15.703$ Å, and the space group is $P6_3/mmc$ (No. 194). The density calculated for two formula units

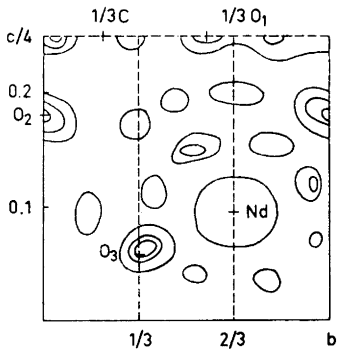

Fig. 3. Fourier projection in the [100] direction of a part of the unit cell.

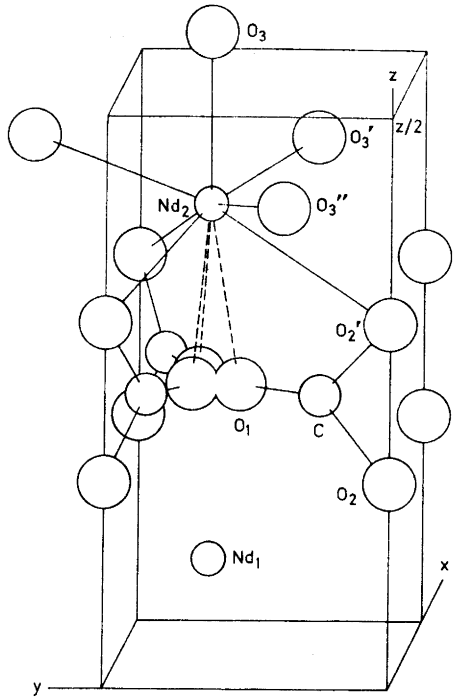

Fig. 4. Axonometric drawing of a part of the unit cell of $Nd_2O_2CO_3$ (type II). The three possible positions of the carbonate ion are indicated.

in the unit cell is 5.89 g/cm^3. The absorption coefficient for Mo-radiation is 239 cm^{-1}. The structure factors for the oxygen and for the carbon atoms were calculated using atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography*. The structure factors for the neodymium atoms were calculated from tables of X-ray scattering factors computed from numerical Hartree-Fock wave functions by Cromer and Mann [6] and from tables of X-ray scattering factors computed from relativistic Dirac-Slater wave function by Cromer and Waber.[7] Average values of these two tables were used and anomalous dispersion correction for the scattering factors was made using only the real part for the correction as given in *International Tables X-ray Crystallography*, Vol. III. The atomic scattering factors were approximated by Bassi [8] polynomials. Atomic coordinates and temperature factors are given in Table 2 and interatomic distances and bond angles in Table 3. A list of observed and calculated structure factors is given in Table 4. Fig. 4 is an axonomeric drawing of a part of the unit cell.

Table 2. Atomic coordinates and temperature factors with standard deviations. Diffractometer data, 124 reflections, $R=5.0$ %.

Atom	x	y	z	B (Å²)
C	0.13 (3)	0.26 (4)	$\frac{1}{2}$	3.1 (1.3)
O_1	0.28 (3)	0.56 (5)	$\frac{1}{4}$	6.5 (4.0)
O_2	0	0	0.178 (3)	2.2 (7)
O_3	$\frac{1}{3}$	$\frac{2}{3}$	0.557 (2)	1.0 (5)
Nd_1	$\frac{1}{3}$	$\frac{2}{3}$	0.0944(1)	0.47 (3)

Table 3. Interatomic distances (Å) and bond angles (degrees) with standard deviations.

C $-O_1$	1.02 (22)	O_1-C-O_2	128 (6)
C $-O_2$	1.45 (10)	O_2-C-O_2'	103 (9)
O_2-O_2'	2.27 (6)		
O_1-O_2	2.23 (14)		
Nd_1-O_1	2.47 (3)	$O_2-Nd_2-O_2'$	75.6 (8)
Nd_1-O_2	2.64 (2)	$O_2'-Nd_2-O_3''$	114.0 (4)
Nd_2-O_3	2.37 (3)	$O_3'-Nd_2-O_2'$	72.7 (6)
O_3-O_3''	2.91 (3)		
$O_3'-O_2'$	2.98 (3)		

Table 4. Observed and calculated structure factors ($\times 10$).

h	k	l	Fo	Fc
0	0	4	712	-669
0	0	6	917	-925
0	0	8	79	-70
0	0	10	619	640
0	0	12	529	504
0	0	14	340	-314
0	0	16	456	-505
0	0	18	156	-131
0	0	20	358	356
0	1	0	440	-459
0	1	1	486	508
0	1	2	332	-306
0	1	3	739	706
0	1	4	336	309
0	1	5	73	88
0	1	6	502	515
0	1	7	677	-696
0	1	9	504	-521
0	1	10	313	-312
0	1	11	154	169
0	1	12	164	-184
0	1	13	571	591
0	1	15	244	268
0	1	16	257	272
0	1	17	242	-268
0	1	19	357	-401
0	1	20	163	-187
0	2	0	372	-394
0	2	1	355	-369
0	2	2	225	-206
0	2	3	669	-622
0	2	4	276	247
0	2	6	402	416
0	2	7	582	554
0	2	9	462	468
0	2	10	292	-269
0	2	11	163	-159
0	2	12	172	-175
0	2	13	523	-514
0	2	14	95	95
0	2	15	224	-249
0	2	16	243	242
0	2	17	231	250
0	2	18	99	65
0	2	19	361	362
0	3	0	714	714
0	3	2	258	253
0	3	4	485	-451
0	3	6	563	-535
0	3	8	75	-41
0	3	10	470	481
0	3	12	314	334
0	3	14	189	-209
0	4	0	223	-246
0	4	1	214	234
0	4	2	127	-114
0	4	3	408	395
0	4	4	191	168
0	4	6	230	240
0	4	7	375	-356
0	4	9	323	-309
0	4	10	187	-190
0	4	11	145	101
0	4	12	108	-125
1	1	0	1046	1066
1	1	2	323	322
1	1	4	571	-589
1	1	6	705	-709
1	1	8	67	-68
1	1	10	580	585
1	1	12	439	421
1	1	14	277	-263
1	1	16	458	-473
1	1	18	124	-113
1	2	0	324	-336
1	2	1	314	330
1	2	2	174	-171
1	2	3	519	528
1	2	4	238	223
1	2	5	70	67
1	2	6	326	345
1	2	7	486	-492
1	2	9	419	-406
1	2	10	272	-245
1	2	11	140	132
1	2	12	147	-160
1	2	13	477	471
1	2	14	95	88
1	2	15	209	220
1	2	16	213	221
1	2	17	215	-224
1	3	0	294	-270
1	3	1	260	-252
1	3	2	119	-128
1	3	3	404	-439
1	3	4	176	184
1	3	5	59	-49
1	3	6	270	266
1	3	7	378	386
1	3	9	359	342
1	3	10	216	-207
1	3	11	150	-114
1	3	12	137	-135
1	3	13	575	-586
1	3	14	106	76
1	4	0	490	466
1	4	2	190	170
1	4	4	326	-303
1	4	6	393	-375
2	2	0	623	634
2	2	2	236	221
2	2	4	409	-398
2	2	6	496	-490
2	2	10	427	435
2	2	12	307	308
2	2	14	221	-193
2	3	0	235	-221
2	3	1	216	213
2	3	2	110	-108
2	3	3	381	363
2	3	4	168	160
2	3	5	75	46
2	3	6	182	213
2	3	7	302	-325

DISCUSSION

The investigation shows that single crystals of type II $Nd_2O_2CO_3$ can be prepared from freshly precipitated neodymium hydroxide and a solution of carbon dioxide in water, using the hydrothermal technique. The crystal structure investigation confirmed the structure suggested in Ref. 1. The structure comprises fairly regular NdO_8 rhombohedra packed in a hexagonal layer of composition $(Nd_2O_2^{2+})_n$. The layers are held together by carbonate ions. Four oxygen atoms occupy the sites *e* of space group $P6_3mmc$, and two are statistically arranged over the sites *h*. The carbon atoms are similarly arranged statistically over sites *h*. The carbonate ion has the C_{2v} symmetry (Fig. 5); however, the two carbon-oxygen distances in the carbonate ion of

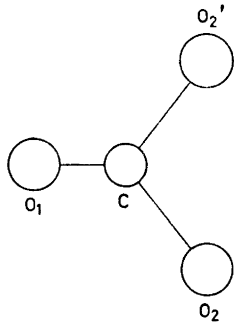

Fig. 5. Projection of the carbonate ion in the structure. The carbon atom C and the oxygen atom O_1 are placed in positions with the symmetry C_{2v}.

1.02(22) Å and 1.45(10) Å are not significantly different from each other, and the oxygen-oxygen distances in the carbonate ion of 2.27(6) Å and 2.23(14) Å are in good agreement with oxygen-oxygen distances in carbonate ions of 2.24 Å, previously reported.[1]

The oxygen atom O_3 is coordinated with four neodymium atoms, forming a fairly regular tetrahedron with an Nd–O–Nd angle of 104.4(8)° and a neodymium-oxygen distance of 2.37(3) Å. The oxygen atom O_1 is coordinated with two neodynium atoms, and the neodymium-oxygen distance is 2.47(3) Å. The oxygen atom O_2 is coordinated with three neodynium atoms, the oxygen-neodymium distance is 2.64(2) Å. These distances are comparable with neodymium-oxygen distances previously reported as in the structure of a neodymium oxydiacetate compound comprising nine coordinated neodymium atoms with distances of 2.37(2) Å and 2.52(3) Å.[9]

Acknowledgements. I am indebted to *Carlsberg Fonden* for use of the diffractometer, to Dr. J. Danielsen, Mrs. R. G. Hazell and Mr. J. Nyborg for the use of some of their ALGOL programs, and to Professor S. Broderson of the Department of Chemical Physics, Aarhus University, for the use of the spectrophotometer.

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Received January 19, 1970.