

The Crystal Structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$

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The isomorphous compounds $\text{Ho}_2(\text{OH})_4\text{CO}_3$, $\text{Er}_2(\text{OH})_4\text{CO}_3$, and $\text{Yb}_2(\text{OH})_4\text{CO}_3$ were prepared by hydrothermal technique and the crystal structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ was solved by direct methods from single crystal X-ray diffraction data. The positions of the hydrogen atoms were determined from a neutron diffraction powder pattern.

$\text{Ho}_2(\text{OH})_4\text{CO}_3$ is monoclinic, space group $P2_1/c$ (No. 14) with $a=6.274(2)$, $b=6.041(1)$, $c=15.416(4)$ Å, $\beta=97.38(2)^\circ$, $Z=4$, and $d_x=5.25$ g cm^{-3} . One holmium atom is coordinated with seven and one with eight oxygen atoms. The structure is a layer structure where the layers are held together by the carbonate ions and by hydrogen bonds. The structure also has non-hydrogen bonded OH-ions.

Freshly precipitated rare earth hydroxide gels react readily with carbon dioxide from the atmosphere, and when such gels are treated hydrothermally, crystalline rare earth oxide carbonates or rare earth hydroxycarbonates are formed.^{1,2} A hydrothermal investigation of the system $\text{Y}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ in the temperature range 250–700 °C at pressures up to 300 MPa yielded the hexagonal $\text{Y}_2\text{O}_2\text{CO}_3$ in the temperature range 600–700 °C. At lower temperatures (250–300 °C) a hydroxycarbonate was formed, and its powder pattern was reported in Ref. 2 (called phase I in Ref. 2). From a preliminary single crystal X-ray structure investigation,¹ the composition of the compound was assumed to be $\text{Y}_2\text{O}(\text{OH})_2\text{CO}_3$. However, the crystal structure of the isomorphous holmium compound reported below shows that the correct composition of the compound is $\text{Y}_2(\text{OH})_4\text{CO}_3$. At least three structure types of rare earth hydroxycarbonates are known, the hexagonal structure of NdOHCO_3 ,³

the orthorhombic structure of YOHCO_3 ,⁴ and that of $\text{Ho}_2(\text{OH})_4\text{CO}_3$.

EXPERIMENTAL

Chemistry. The crystalline compounds were synthesized hydrothermally in pressure vessels lined with silver or gold.² The rare earth carbonates of Ho, Er, and Yb were precipitated from solutions made by dissolving the respective oxides in nitric acid, with a 1 M KHCO_3 solution, and the precipitates were washed with water and treated with a 0.33 M KHCO_3 solution at 300 °C and 7.5 MPa for 50 h. The products were washed with water and dried in air at room temperature. The rare earth contents of the compounds were determined by EDTA titrations.⁵ (Found: Ho 72.0. Calc. for $\text{Ho}_2(\text{OH})_4\text{CO}_3$: 72.0. Found: Er 72.8. Calc. for $\text{Er}_2(\text{OH})_4\text{CO}_3$: 72.3. Found: Yb 72.8. Calc. for $\text{Yb}_2(\text{OH})_4\text{CO}_3$: 73.0).

The infra red spectra of $\text{Ho}_2(\text{OH})_4\text{CO}_3$, $\text{Er}_2(\text{OH})_4\text{CO}_3$, and $\text{Yb}_2(\text{OH})_4\text{CO}_3$ were recorded with a Perkin Elmer 521 spectrometer in the frequency range 4000 to 400 cm^{-1} . Pellets of CsI containing 1 % of the compounds were used in the measurements. The spectra of the three compounds were very similar and that of $\text{Er}_2(\text{OH})_4\text{CO}_3$ is displayed in Fig. 1.

X-Ray diffraction. Guinier photographs of the compounds were taken with NaCl ($a=5.6389$ Å) or Si ($a=5.43050$ Å) as internal standards using a Guinier camera with $\text{CuK}\alpha_1$ radiation ($\lambda=1.54051$ Å). The positions and intensities of the diffraction lines were measured on a double beam photometer, and from the indexed powder patterns the unit cell parameters were derived by a least-squares procedure using the program CELREF.⁶ Table 1 gives a list of the parameters obtained.

A single crystal of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ with the dimensions $0.10 \times 0.10 \times 0.03$ mm was selected for

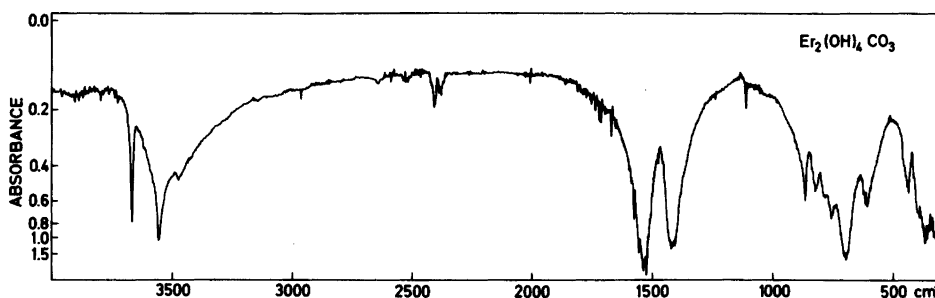


Fig. 1. Infra red spectrum of $\text{Er}_2(\text{OH})_4\text{CO}_3$.

the structure investigation. The X-ray diffraction data were measured on an automatic four-circle diffractometer (Picker) using $\text{MoK}\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$), and using an $\omega-2\theta$ step-scan technique with a total scan width of $2.0^\circ + \tan \theta \cdot 0.692^\circ$ in 2θ . The extent of the peak was decided by the minimum $\sigma(I)/I$ method.⁷ 3979 reflections were measured, corrected for absorption⁸ ($\mu=281 \text{ cm}^{-1}$), and averaged to give 1841 independent reflections of which the 894 which had $I>3\sigma(I)$ were used in the refinements.

Neutron diffraction. The neutron diffraction powder pattern of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ was measured at the spectrometer DIB at the Institute Max von Laue–Paul Langevin in Grenoble using 2.5186 \AA neutrons. The powder was housed in an 8 mm diameter vanadium container and the pattern was measured in the θ -range from 8.0 to 47.8° . The measuring time for the spectrum was 18 h.

STRUCTURE DETERMINATION

The structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ was solved using the program MULTAN⁹ that gave one solution phased on 1040 phase relationships with the positions of six of the ten non-hydrogen atoms in the asymmetric unit of space group $P2_1/c$. The structure factors were calculated with the atomic scattering curves reported by Cromer

and Mann¹⁰ and the scattering contributions for the holmium atoms were corrected for anomalous dispersion.¹¹ The positional parameters of the atoms were refined and the remaining non-hydrogen atoms were found in a difference Fourier map. The structure was refined using the least-squares program LINUS¹² and one scale factor, three positional and six anisotropic temperature factor parameters for each of the ten non-hydrogen atoms, and one extinction parameter were varied. At a conventional R -value of 3.8 % the positions of the four hydrogen atoms in the asymmetric unit were calculated and confirmed in a difference Fourier map. The weights used were $w=\sigma(F)^{-2}$ with $\sigma(F)=[\sigma_c(F^2)+1.02F^2]^{1/2}+|F|$, where $\sigma_c(F^2)$ is the standard deviation from the counting statistics. The final R -value of the structure with the hydrogen atoms inserted was 3.7 %. In Table 2 are listed the positional and thermal parameters of the structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$, and Table 3 is a list of interatomic distances. A list of observed and calculated structure factors is available on request.

The neutron diffraction powder pattern of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ was used to refine the atomic positions of the hydrogen atoms in the structure

Table 1. Unit cell parameters of the isomorphous yttrium and rare earth hydroxycarbonates, space group $P2_1/c$ (No. 14). Standard deviations in parentheses.

	a (Å)	b (Å)	c (Å)	β (°)	Ref.
$\text{Y}_2(\text{OH})_4\text{CO}_3$	6.25	6.01	15.40	97.5	2
$\text{Ho}_2(\text{OH})_4\text{CO}_3$	6.274(2)	6.041(1)	15.416(4)	97.38(2)	This work
$\text{Er}_2(\text{OH})_4\text{CO}_3$	6.249(2)	6.007(1)	15.340(3)	97.46(2)	This work
$\text{Yb}_2(\text{OH})_4\text{CO}_3$	6.212(2)	5.942(2)	15.220(4)	97.61(3)	This work

Table 2. Atomic coordinates and anisotropic temperature factor parameters ($\times 10^4$) of $\text{Ho}_2(\text{OH})_4\text{CO}_3$. Standard deviations in parentheses. Hydrogen atom positions are from the neutron diffraction data.

Atom	x	y	z	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ho1	0.5905(2)	0.2485(2)	0.0665(1)	82(5)	53(6)	87(9)	3(3)	12(6)	7(3)
Ho2	0.5794(2)	0.2360(2)	0.3189(1)	117(6)	48(5)	76(8)	1(5)	25(6)	3(5)
O1	0.698(4)	0.888(3)	0.376(2)	179(102)	115(88)	315(137)	15(73)	165(100)	125(87)
O2	0.956(4)	0.118(3)	0.356(2)	196(103)	64(81)	258(133)	-23(70)	17(94)	4(82)
O3	0.375(4)	0.132(3)	0.440(1)	222(101)	135(89)	78(100)	9(79)	29(82)	4(75)
O4	0.680(3)	0.453(3)	0.448(2)	95(83)	86(81)	143(116)	-4(66)	8(78)	17(79)
O5	0.691(4)	0.497(4)	0.231(2)	148(99)	176(100)	269(147)	114(78)	93(100)	106(93)
O6	0.963(3)	0.282(4)	0.088(2)	152(86)	149(94)	378(134)	-103(80)	39(87)	-177(102)
O7	0.668(4)	0.027(3)	0.189(2)	117(90)	136(87)	109(116)	-20(70)	-1(86)	25(79)
C1	0.099(4)	0.424(4)	0.117(2)	167(125)	72(103)	94(125)	-31(89)	31(103)	-14(95)
H3	0.206(5)	0.172(5)	0.430(2)	0.8(2)					
H4	0.800(5)	0.524(7)	0.447(2)	0.8(2)					
H5	0.819(4)	0.531(9)	0.208(2)	0.8(2)					
H7	0.196(6)	0.487(8)	0.305(2)	0.8(2)					

^a B (\AA^2) for the hydrogen atoms.

Table 3. Interatomic distances (\AA) of $\text{Ho}_2(\text{OH})_4\text{CO}_3$. Standard deviations are 0.02 for Ho–O bonds, 0.03 \AA for other bonds.

Ho1–O1'	2.280	Ho2–O1''	2.366	C1–O1'	1.274
O3'	2.336	O2	2.461	O2'	1.318
O3''	2.331	O3	2.494	O6'	1.245
O4'	2.463	O4	2.396		
O4''	2.334	O5	2.252		
O6	2.329	O5'	2.284		
O7	2.318	O7	2.492		
		O7'	2.343		

Hydrogen bonds

O3–H3...O2''' 2.776

O5–H5...O2'' 2.836

using the Hewat version of the Rietveld profile refinement program.^{13,14} The scattering lengths used for the four atoms were: Ho: 0.837, O: 0.5805, C: 0.661, and H: -0.3741, all in units of 10^{-12} cm.¹⁵ The parameters refined were three positional parameters of each of the four hydrogen atoms, one overall temperature factor, one scale factor, three profile parameters, one zero point parameter, and four unit cell parameters, giving a total of 22 parameters. The positional parameters for the hydrogen atoms arrived at for a conventional *R*-value of 8.5 % are listed in Table 2. The values agree well with the values calculated assuming that the oxygen atoms O3,

O4, and O7 are coordinated tetrahedrally by three holmium atoms and one hydrogen atom, and that the oxygen atom O5 has an sp^2 -type bonding arrangement to two holmium atoms and one hydrogen atom. A list of observed and calculated intensities of the neutron diffraction powder pattern is available on request.

DISCUSSION

The crystal structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ has Ho1 coordinated in a HoO_7 polyhedron and Ho2 coordinated in a HoO_8 polyhedron (Fig. 2). It is not very often that two types of coordination

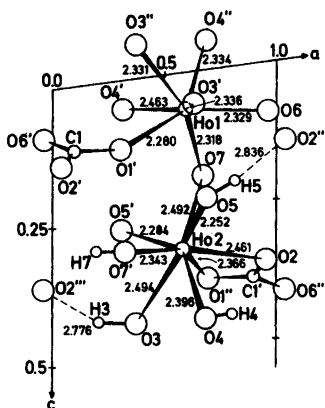


Fig. 2. The HoO_7 and HoO_8 coordination polyhedra and the carbonate ion in the structure. For simplicity the polyhedra with holmium in $y=3/4$ have been omitted.

polyhedra of the rare earth ion are found in simple rare earth compounds. In the structure of $\text{NaHo}_4(\text{GeO}_4)_2\text{O}_2\text{OH}^{16}$ the two holmium atoms are seven coordinated with oxygen atoms. The polyhedra in $\text{Ho}_2(\text{OH})_4\text{CO}_3$ are packed together in a layer parallel to the bc -plane of the unit cell, and the structure is thus a layer structure (Fig. 3) which is not unusual for rare earth compounds.¹⁷ The layers are held together by the carbonate ions and by the hydrogen bonds $\text{O5}-\text{H5}\cdots\text{O2}$ and $\text{O3}-\text{H3}\cdots\text{O2}$. The OH-ions $\text{O7}-\text{H7}$ and

$\text{O4}-\text{H4}$ are not involved in hydrogen bonds. This situation is also reflected in the infra red spectrum of the compound (Fig. 1) that has the characteristic frequency of a non-hydrogen bonded OH-group at 3670 cm^{-1} and frequencies at 3550 and 3470 cm^{-1} corresponding to hydrogen bonded OH-groups.

The interatomic holmium-oxygen distances in the two coordination polyhedra are in good agreement with the $\text{Ho}-\text{O}$ distances found in other holmium compounds. For HoOOH^{18} the $\text{Ho}-\text{O}$ distances are from $2.25(6)$ to $2.47(5)\text{ \AA}$, and for $\text{NaHo}_4(\text{GeO}_4)_2\text{O}_2\text{OH}^{16}$ the $\text{Ho}-\text{O}$ distances are from $2.20(2)$ to $2.55(2)\text{ \AA}$.

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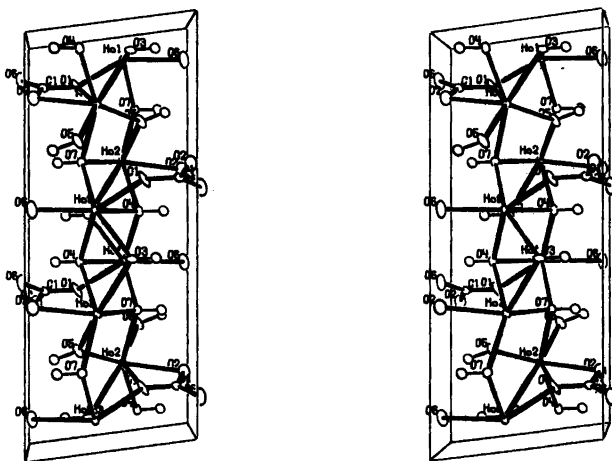


Fig. 3. Three-dimensional model of the crystal structure of $\text{Ho}_2(\text{OH})_4\text{CO}_3$. Same orientation as in Fig. 2.

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