

Crystal chemistry of RE(CO₃)OH

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Abstract. Rare earth carbonate hydroxides, RE(CO₃)OH, were hydrothermally synthesized from formic acid and the hydroxide gels of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y. An orthorhombic phase with a kozoite-type structure was obtained for RE = Nd and Sm. Another orthorhombic modification of the kozoite-type structure was obtained for RE = Eu, Gd, Tb, Dy, Ho, Er, Tm, and Y. The latter phase has a lower symmetry (space group: $P2_12_12_1$) in comparison to the true kozoite-type structure ($Pnma$). A new tetragonal phase (space group: $P4_2/nmc$) was found for RE = Tm and Yb.

The crystal structures of RE(CO₃)OH were refined for $Pnma$ (RE = Nd and Sm), $P2_12_12_1$ (RE = Eu, Gd, Tb, Dy, Ho, Er, Tm and Y), and $P4_2/nmc$ phases (RE = Tm and Yb) using single-crystal X-ray diffraction intensity data. The distinct features of the differences among the three structures are the coordination numbers of the RE³⁺ ions: 10, 9, and 8 for the $Pnma$, $P2_12_12_1$, and $P4_2/nmc$ phases, respectively. A systematic comparison of the two orthorhombic structures revealed a dynamic variation in the coordination environment of the RE³⁺ ions accompanied by variations in their ionic radii. Although the interatomic RE–O distances tend to decrease with the lanthanide contraction, exceptions were observed for two of the RE–O distances. The mutual close proximity of CO₃²⁻ anions caused by the lanthanide contraction led to repulsion between the CO₃²⁻ anions, which decreased the symmetry of the configuration of CO₃²⁻ anions around the central RE³⁺ ion, and some oxygen atoms of CO₃²⁻ moved away from the first coordination shell of the RE³⁺ ions due to the elongation of the RE–O distances.

The crystal structures of the tetragonal RE(CO₃)OH are distinct from those of the orthorhombic phases. They consist of ladders of RE³⁺ ions 8-coordinated by the CO₃²⁻ and OH⁻ anions arranged in the form of a double cross. The powder XRD patterns of the tetragonal RE(CO₃)OH are identical to that of a synthetic material previously reported as Tm₆(OH)₄(CO₃)₇.

Introduction

The hydroxyl carbonates of rare earth elements, RE(CO₃)OH, are the major compounds among rare earth carbonates as well as the hydrous carbonates of the rare earth elements, RE₂(CO₃)₃ · nH₂O. They are described as rare earth basic carbonates, and some of them occur as mineral species in nature. Two polymorphs are well known as rare earth carbonate hydroxides (RE(CO₃)OH); one of them is hexagonal and the other is orthorhombic (Dexpert and Caro, 1974). The hexagonal phase occurs as minerals, hydroxylbastnäsite-(Ce) (Kirillov, 1964) and hydroxylbastnäsite-(Nd) (Maksimović and Pantó, 1985; Farkas *et al.*, 1985). These mineral species are the (OH)-analogs of bastnäsite-(Ce), Ce(CO₃)F, which is well known as the major ore mineral for the rare earth elements. On the other hand, the orthorhombic RE(CO₃)OH was first reported as a synthetic phase, and its crystal structure has also been reported (Dexpert and Caro, 1974). Recently, natural occurrences of the orthorhombic phases have been reported as new minerals: kozoite-(Nd) (Miyawaki *et al.*, 2000) and kozoite-(La) (Miyawaki *et al.*, 2003). These orthorhombic phases are isostructural with the ancylite group minerals: ancylite-(Ce) CeSr(CO₃)₂(OH) · H₂O (Dal Negro *et al.*, 1975), calcioancylite-(Ce) CeCa(CO₃)₂(OH) · H₂O (Orlandi *et al.*, 1990), gysinite-(Nd) NdPb(CO₃)₂(OH) · H₂O (Chabot and Sarp, 1985), etc. These minerals tend to enrich in the larger light rare earth elements such as Ce and Nd, as described below.

Many synthetic studies of RE(CO₃)OH have involved hydrothermal reactions. Chai *et al.* (1978) reported the single crystal growth of hexagonal RE(CO₃)OH (RE = Y, La, Gd, and Er) using NH₄Cl and K₂CO₃ as crystallizers. Kutty *et al.* (1984) synthesized several rare earth carbonate hydroxides with oxalic acid. Tareen *et al.* (1980) reported the single crystal growth of orthorhombic Y(CO₃)OH using formic acid.

A few other polymorphs have been reported as synthetic materials with different space groups. Christensen (1973) analyzed the crystal structure of hexagonal Nd(CO₃)OH and reported the space group to be $P\bar{6}$ instead of $P\bar{6}2c$ the space group for the bastnäsite structure. Kutlu and Meyer (1999) determined the crystal structure of hexagonal Dy(CO₃)OH with the space group of $P\bar{6}$. These two results show a slight difference in the configuration of the carbonate ions around the rare earth ions. No structure data for

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Table 1. Experimental conditions for hydrothermal syntheses and reaction products.

RE	Condition of reaction			Reaction product	
	Temperature (°C)	Pressure (atm)	Conc. of formic acid (%)	Crystal system	Space group
Nd	220	50	10	Orthorhombic	<i>Pnma</i>
Sm	220	500	10	Orthorhombic	<i>Pnma</i>
Eu	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Gd	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Tb	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Dy	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Y	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Ho	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Er	220	500	10	Orthorhombic	<i>P2₁2₁2₁</i>
Tm	220	500	5	Orthorhombic	<i>P2₁2₁2₁</i>
Tm	220	500	10	Tetragonal	<i>P4₂/nmc</i>
Yb	220	500	10	Tetragonal	<i>P4₂/nmc</i>

hexagonal RE(CO₃)OH phases have been reported for the other rare earths. Other orthorhombic RE(CO₃)OH phases with the *P2₁2₁2₁* space group have been described for RE = Y (Beall *et al.*, 1976) and for RE = Dy (Doert *et al.*, 1999).

The formation of individual phases is affected by differences in the ionic radii of the rare earths. The hexagonal phases were synthesized using the light rare earth elements (La–Gd), but the orthorhombic phases with the entire series of lanthanides including the heavy rare earth elements (Gd–Lu). Some new rare earth carbonate phases have been reported for RE = Tm, Yb, and Lu (Kutty *et al.*, 1984), with their formulae being given as RE₂O(CO₃)(OH)₂, RE₆(CO₃)₇(OH)₄, RE₆(CO₃)₃(OH)₈, RE₄(CO₃)₃(OH)₆, and RE₁₂O₇(CO₃)₆(OH)₁₀, which are not equivalent to the ordinary RE(CO₃)(OH).

In this study, two types of orthorhombic phases and a new tetragonal polymorph of RE(CO₃)OH were hydrothermally synthesized using formic acid as the solvent and a mineralizer, and their structures were analyzed by the single crystal X-ray diffraction method. Variations in their crystal structures accompanied by the lanthanide contraction, and the relationships among the three structures are discussed from the perspective of crystal chemistry in this report.

Experimental methods

Hydrothermal synthesis

The starting materials are rare earth hydroxide gels. An aqueous solution of ammonia was dropped into an aqueous solution of the rare earth nitrate, and the two were mixed with a stirrer to obtain the hydroxide gel. The precipitated gel was washed with distilled water to remove any soluble components. The gel was then dried in an electric oven and ground into a fine powder. Approximately 50 mg of the starting powder was charged into a platinum ampoule (50 mm length, 2.7 mm ID) with 0.1 ml of formic acid (5 or 10% concentration). The ampoule was immediately sealed using a micro-welder. The sealing of the am-

poule was checked under a microscope in order to avoid any leaking out of the starting materials. The hydrothermal synthesis was carried out using a test tube type bomb with water as the pressurizing fluid at 220 °C at a pressure of 50 or 500 kg/cm². The duration of the hydrothermal run was fixed at 4 days. The bomb was air-quenched to room temperature after the run. The synthetic product was washed with distilled water and dried in an air oven at 100 °C. The experimental conditions for the hydrothermal syntheses are summarized in Table 1.

Crystallography

The single crystals of RE(CO₃)OH suitable for the X-ray diffraction experiments were selected, mounted on glass fibers, and placed on the goniometer heads. The crystal data were obtained using a Bruker SMART APEX CCD area-detector diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). The intensity data were collected using the ω -scan technique. The data reduction and correction for the factors of Lorentz and polarization and for the background effects were carried out using the program SAINTPLUS. The empirical collection for absorption based on symmetrically equivalent reflections was performed with SADABS software (Sheldrick, 1997). The structures were solved by a direct method and expanded with a Fourier technique using the SHELXTL (Sheldrick, 1996) program. The atomic displacement parameters were refined except for the hydrogen atoms.

Results and discussion

Orthorhombic RE(CO₃)OH

The hydroxyl carbonates RE(CO₃)OH of Nd and Sm crystallize in space group *Pnma*, and they are isostructural with kozoite-(Nd). In contrast, the orthorhombic phases of Y, Eu, Gd, Tb, Dy, Ho, Er, and Tm show a lower symmetry with space group *P2₁2₁2₁*, which has been reported for Y(CO₃)OH (Beall *et al.*, 1976) and Dy(CO₃)OH (Doert *et al.*, 1999). These structures, however, are closely related

Table 2. Crystal data and results of structure refinements with final atomic positional parameters and equivalent isotropic displacement parameters for RE(CO₃)OH.

	Nd	Sm	Eu	Gd	Tb	Dy	
Unit cells by least squares							
<i>Orthorhombic phase</i>							
space group	<i>Pnma</i>	<i>Pnma</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	
<i>a</i> (Å)	7.2333(9)	7.1388(6)	7.1002(9)	7.0755(7)	7.0256(8)	6.9813(6)	
<i>b</i> (Å)	4.9640(6)	4.9151(4)	4.8932(6)	4.8739(5)	4.8577(6)	4.8336(4)	
<i>c</i> (Å)	8.4908(11)	8.4717(8)	8.4530(11)	8.4471(9)	8.4657(10)	8.4449(8)	
<i>V</i> (Å ³)	304.87(7)	297.25(4)	293.68(6)	291.30(5)	288.92(6)	284.97(4)	
<i>Z</i>	4	4	4	4	4	4	
Collected refl.	1868	1817	1657	1608	1961	1859	
Unique refl.	394	381	670	716	710	645	
<i>R</i> 1 (<i>I</i> > 2σ)	0.0251	0.0146	0.0161	0.0156	0.0148	0.0130	
<i>wR</i> 2 (<i>I</i> > 2σ)	0.0493	0.0379	0.0366	0.0320	0.0328	0.0294	
<i>R</i> 1	0.0288	0.0147	0.0164	0.0168	0.0149	0.0131	
<i>wR</i> 2	0.0503	0.0380	0.0367	0.0324	0.0329	0.0295	
Largest peaks on difference maps (e/Å³)							
(+)	0.993	1.115	0.729	0.849	0.624	0.786	
(-)	1.929	0.812	1.234	0.662	0.582	0.479	
Atomic positions							
RE	<i>x</i>	0.35557(6)	0.35839(3)	0.14042(3)	0.13966(3)	0.13696(3)	0.13621(2)
	<i>y</i>	0.25	0.25	0.24748(7)	0.24592(7)	0.24456(5)	0.24327(5)
	<i>z</i>	0.66625(5)	0.66508(3)	0.08456(2)	0.08493(3)	0.08608(2)	0.08620(2)
	<i>U</i> _{eq} (Å ²)	0.00776(18)	0.00868(15)	0.00796(12)	0.00829(9)	0.00813(10)	0.00864(10)
C	<i>x</i>	0.3042(10)	0.3017(8)	0.1997(6)	0.1994(6)	0.2010(5)	0.2004(5)
	<i>y</i>	0.25	0.25	0.2461(15)	0.2455(16)	0.2473(13)	0.2471(12)
	<i>z</i>	0.3206(9)	0.3228(6)	0.4257(5)	0.4242(5)	0.4236(5)	0.4221(5)
	<i>U</i> _{eq} (Å ²)	0.0070(14)	0.0092(10)	0.0079(8)	0.0093(8)	0.0079(7)	0.0090(8)
O1	<i>x</i>	0.0364(8)	0.0393(5)	0.9588(4)	0.9586(4)	0.9560(4)	0.9558(4)
	<i>y</i>	0.25	0.25	0.2515(13)	0.2509(12)	0.2515(11)	0.2518(10)
	<i>z</i>	0.6035(7)	0.6064(5)	0.8584(3)	0.8588(4)	0.8624(4)	0.8627(3)
	<i>U</i> _{eq} (Å ²)	0.0137(13)	0.0141(8)	0.0126(6)	0.0128(6)	0.0139(6)	0.0130(6)
O2	<i>x</i>	0.2936(8)	0.2949(6)	0.2033(5)	0.2025(4)	0.2009(4)	0.2000(4)
	<i>y</i>	-0.25	-0.25	0.7466(11)	0.7453(13)	0.7428(10)	0.7400(10)
	<i>z</i>	0.6962(6)	0.6970(5)	0.0510(4)	0.0503(4)	0.0487(4)	0.0482(4)
	<i>U</i> _{eq} (Å ²)	0.0125(12)	0.0143(8)	0.0128(6)	0.0134(6)	0.0135(6)	0.0138(6)
O3	<i>x</i>	0.6521(5)	0.6536(3)	0.8399(8)	0.846(10)	0.8403(9)	0.8398(8)
	<i>y</i>	-0.0253(8)	-0.0241(6)	0.5170(8)	0.5160(8)	0.5128(8)	0.5109(7)
	<i>z</i>	0.6129(5)	0.6107(3)	0.1371(6)	0.1377(6)	0.1379(5)	0.1379(5)
	<i>U</i> _{eq} (Å ²)	0.0105(8)	0.0111(5)	0.0095(10)	0.0099(12)	0.0101(9)	0.0106(9)
O4	<i>x</i>			0.8536(9)	0.8479(11)	0.8507(10)	0.8502(9)
	<i>y</i>			0.9698(8)	0.9689(8)	0.9682(7)	0.9681(7)
	<i>z</i>			0.1459(6)	0.1462(7)	0.1504(5)	0.1509(5)
	<i>U</i> _{eq} (Å ²)			0.0108(10)	0.0125(12)	0.0125(9)	0.0130(9)

to kozoite-(Nd), as will be described later. Figure 1 shows the variation in the lattice parameters of the orthorhombic RE(CO₃)OH as a function of the ionic radii of the RE³⁺ ions (RE = Nd to Tm). While the *a* and *b* parameters continuously decrease with the decreases in the RE ionic radius, the *c* parameters do not show any specific trend.

The crystal structures of Nd(CO₃)OH and Sm(CO₃)OH with space group *Pnma* consist of carbonate groups (C,

O2, O3, and O3') and hydroxyl groups (O1) bonded to the Nd or Sm ions. In the crystal structures, the OH ions connect the cations to form zigzag chains of $\frac{1}{\infty}[(\text{OH})\text{RE}_{2/2}]^{2+}$ running along [100]. The chains are linked by the CO₃ ions (Fig. 2). The coordination about the Nd in the *Pnma* phase is shown in Fig. 3a. The Nd or Sm atom is coordinated by ten oxygen atoms (two from the OH and eight from the CO₃), forming a polyhedron, which can be de-

Table 2. (continued)

	Y	Ho	Er	Tm	Tm	Yb	
Unit cells by least squares							
	<i>Orthorhombic phase</i>				<i>Tetragonal phase</i>		
space group	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>	<i>P4₂/nmc</i>	<i>P4₂/nmc</i>	
<i>a</i> (Å)	6.9591(6)	6.9583(9)	6.9386(12)	6.9028(6)	9.3951(4)	9.3771(7)	
<i>b</i> (Å)	4.8141(4)	4.8121(6)	4.7963(8)	4.7833(4)			
<i>c</i> (Å)	8.4722(8)	8.4558(11)	8.4863(14)	8.5086(8)	7.7546(6)	7.7117(11)	
<i>V</i> (Å ³)	283.83(4)	283.13(6)	282.42(8)	281.57(5)	684.48(7)	678.09(12)	
<i>Z</i>	4	4	4	4	8	8	
Collected refl.	2104	1838	1854	1832	1647	1863	
Unique refl.	708	641	694	640	441	437	
<i>R1</i> (<i>I</i> > 2σ)	0.0263	0.0139	0.0141	0.0147	0.0257	0.0212	
<i>wR2</i> (<i>I</i> > 2σ)	0.0575	0.0316	0.0323	0.0344	0.0631	0.0558	
<i>R1</i>	0.0272	0.0139	0.0146	0.0150	0.0293	0.0235	
<i>wR2</i>	0.0579	0.0317	0.0325	0.0346	0.0652	0.0583	
Largest peaks on difference maps (e/Å³)							
(+)	0.556	1.229	0.997	1.977	1.640	1.562	
(-)	0.598	0.638	0.676	0.716	0.783	1.575	
Atomic positions							
RE	<i>x</i>	0.13406(6)	0.13472(3)	0.13274(3)	0.13041(3)	0.47399(3)	0.47311(2)
	<i>y</i>	0.23847(10)	0.23889(5)	0.23551(4)	0.23451(5)	0.52601(3)	0.52689(2)
	<i>z</i>	0.08630(5)	0.08633(3)	0.08654(2)	0.08702(3)	0.25	0.25
	<i>U</i> _{eq} (Å ²)	0.00710(18)	0.00837(10)	0.00817(9)	0.00804(11)	0.0077(2)	0.0060(2)
C	<i>x</i>	0.2017(6)	0.2012(6)	0.2031(6)	0.2032(8)	0.4966(10)	0.4976(8)
	<i>y</i>	0.2455(11)	0.2440(12)	0.2438(10)	0.2438(14)	0.25	0.25
	<i>z</i>	0.4204(5)	0.4202(6)	0.4191(6)	0.4180(7)	0.0992(11)	0.0995(8)
	<i>U</i> _{eq} (Å ²)	0.0070(8)	0.0088(9)	0.0088(9)	0.0097(10)	0.0078(15)	0.0072(12)
O1	<i>x</i>	0.9539(4)	0.9540(5)	0.9524(5)	0.9506(6)	0.25	0.25
	<i>y</i>	0.2520(10)	0.2529(10)	0.2525(8)	0.2538(12)	0.5132(7)	0.5135(6)
	<i>z</i>	0.8664(4)	0.8641(4)	0.8659(4)	0.8692(5)	0.1672(9)	0.1674(7)
	<i>U</i> _{eq} (Å ²)	0.0118(7)	0.0134(8)	0.0128(7)	0.0127(9)	0.0145(13)	0.0161(11)
O2	<i>x</i>	0.1985(5)	0.1988(5)	0.1980(5)	0.1955(6)	0.4876(8)	0.4866(7)
	<i>y</i>	0.7351(10)	0.7353(10)	0.7299(8)	0.7288(11)	0.25	0.25
	<i>z</i>	0.0449(4)	0.0457(4)	0.0427(4)	0.0421(5)	0.2639(8)	0.2651(6)
	<i>U</i> _{eq} (Å ²)	0.0123(7)	0.0130(8)	0.0128(7)	0.0117(9)	0.0163(14)	0.0151(12)
O3	<i>x</i>	0.8359(6)	0.8367(10)	0.8328(6)	0.8306(7)	0.4953(5)	0.4949(4)
	<i>y</i>	0.5059(8)	0.5055(8)	0.5018(7)	0.4975(10)	0.6314(4)	0.6309(3)
	<i>z</i>	0.1372(5)	0.1371(5)	0.1358(5)	0.1356(5)	-0.0177(5)	-0.0191(4)
	<i>U</i> _{eq} (Å ²)	0.0111(9)	0.0105(10)	0.0111(9)	0.0095(10)	0.0111(8)	0.0110(7)
O4	<i>x</i>	0.8553(7)	0.8554(9)	0.8576(7)	0.8592(8)		
	<i>y</i>	0.9625(7)	0.9623(10)	0.9573(6)	0.9561(9)		
	<i>z</i>	0.1555(5)	0.1557(5)	0.1585(5)	0.1601(6)		
	<i>U</i> _{eq} (Å ²)	0.0110(8)	0.0131(9)	0.0111(7)	0.0118(9)		

scribed as a square antiprism with two additional apexes on the top square table.

The crystal structures of the other orthorhombic RE(CO₃)OH phases with space group *P2₁2₁2₁* can be expressed as distorted kozoite structures. The carbonate ion consisting of C, O2, O3, and O4 does not have a mirror symmetry. A rare earth atom such as Tm is coordinated by nine oxygen atoms (two from the OH and seven from the CO₃) to form a distorted monocapped square antiprism

(Fig. 3b). As can be seen from Fig. 3, the coordination features of RE in the two types of orthorhombic phases are comparable.

Figure 4 shows the relation between RE–O bond length and ionic radius of RE³⁺ for the orthorhombic RE(CO₃)OH phases. The Nd–O distances range from 2.352(6) to 2.747(4) Å (Table 3) and are slightly smaller than those of kozoite-(Nd). This difference may be due to the coexistence of larger La ions substituting for Nd in natural ko-

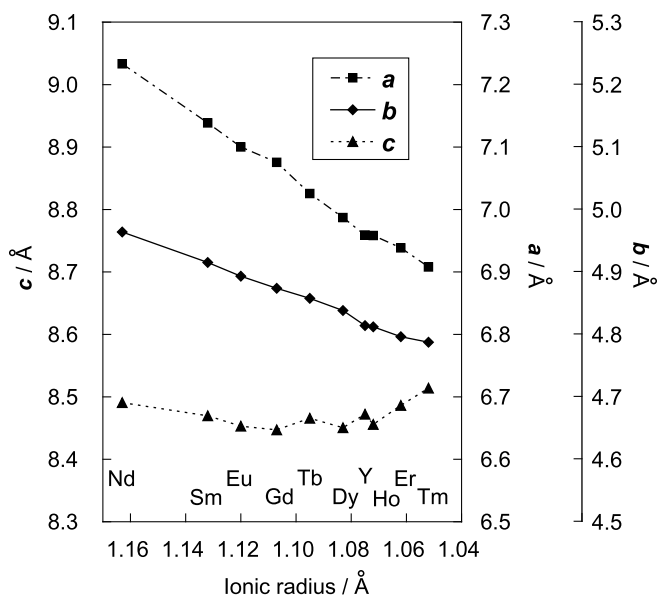


Fig. 1. Variation in lattice parameters for the orthorhombic $\text{RE}(\text{CO}_3)\text{OH}$ phase. The RE radius is from Shannon (1976).

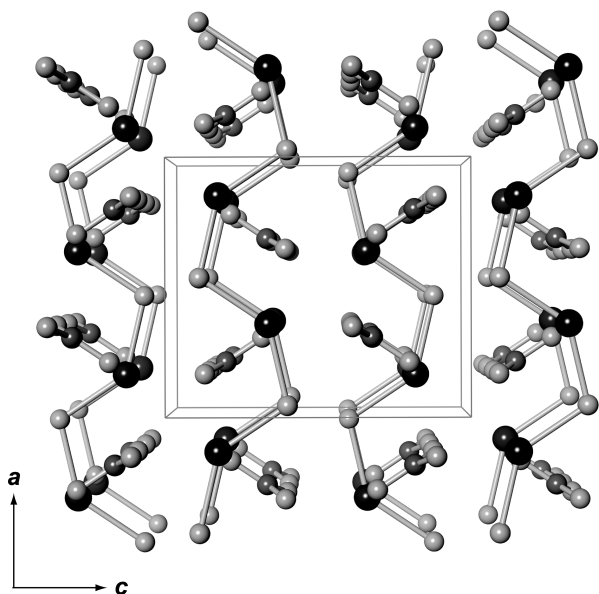


Fig. 2. Projection of the crystal structure of orthorhombic $\text{Nd}(\text{CO}_3)\text{OH}$ onto (010). Black circles represent Nd atoms, dark grey circles represent C atoms, and light grey circles represent O atoms.

zoite-(Nd). The RE–O distance tends to decrease with the lanthanide contraction, except for parts of the RE–O₄ and RE–O₃ distances as shown in Fig. 4. These RE–O bonds without the decreasing trend are roughly parallel to the *c* axis. The exceptional RE–O₄ distance tends to increase with the contraction from RE = Eu to Tm and then expelled from the first coordination sphere of the RE atom. For example, the shorter nine Tm–O distances range from 2.232(4) to 2.632(5) Å (Table 3). The tenth Tm–O distance, 3.018 Å, is too long to be included in the coordination sphere of the Tm ion. This variation is not linear in relation to the contraction and is responsible for the anomaly of the *c* parameters. This nonlinearity can be ascribed to the repulsion between the CO₃ anions involved in the RE-coordination polyhedra, resulting from the shrinkage of the polyhedra due to the lanthanide contraction.

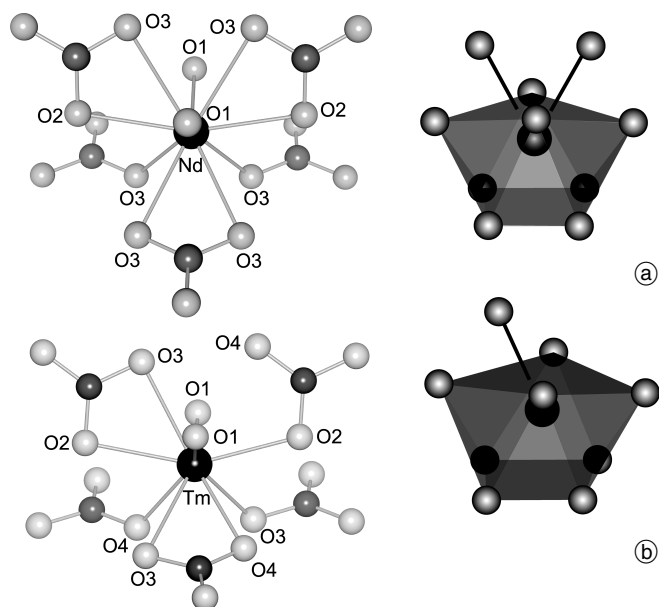


Fig. 3. Coordination polyhedra of rare earth atoms in the orthorhombic $\text{RE}(\text{CO}_3)\text{OH}$. (a) Nd in $\text{Nd}(\text{CO}_3)\text{OH}$ [$Pnma$], (b) Tm in $\text{Tm}(\text{CO}_3)\text{OH}$ [$P2_12_12_1$].

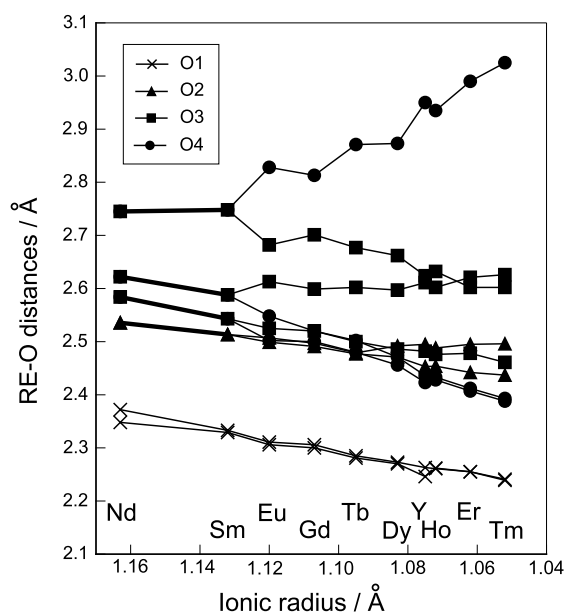


Fig. 4. Variation in RE–O bond distances for the orthorhombic $\text{RE}(\text{CO}_3)\text{OH}$ phases.

The tetragonal $\text{RE}(\text{CO}_3)\text{OH}$

The tetragonal phase is a new polymorph of $\text{RE}(\text{CO}_3)\text{OH}$ in addition to the hexagonal and orthorhombic phases. The powder diffraction data of the tetragonal $\text{Tm}(\text{CO}_3)\text{OH}$ obtained in this study are shown in Table 5. Kutty *et al.* (1984) reported very similar diffraction data for $\text{Tm}_6(\text{OH})_4(\text{CO}_3)_7$, and these data are also shown in the table for comparison. It can be seen that the powder diffraction pattern given by Kutty *et al.* is identical to that of the present tetragonal phase. The correct chemical formula of this phase should be $\text{Tm}(\text{CO}_3)\text{OH}$. The reasonable reliability factor of the crystal structure analysis has confirmed the chemical formula.

The crystal structure of $\text{Tm}(\text{CO}_3)\text{OH}$ consists of carbonate group (C, O₂, O₃, and O_{3'}) and hydroxyl ions

Table 3. Selected bond length (Å) for natural and synthetic orthorhombic RE(CO₃)OH.

	Kozoite-(Nd) ^a		Nd(CO ₃)OH		Sm(CO ₃)OH	
RE–O1	2.38(1)		2.352(6)		2.327(4)	
RE–O1	2.68(1)		2.370(6)		2.332(4)	
RE–O2	2.526(2)	×2	2.5350(12)	×2	2.5136(9)	×2
RE–O3	2.597(6)	×2	2.583(4)	×2	2.543(2)	×2
RE–O3	2.63(1)	×2	2.620(4)	×2	2.588(3)	×2
RE–O3	2.785(8)	×2	2.747(4)	×2	2.749(3)	×2
Mean	2.61		2.569		2.545	
C–O2	1.33(1)		1.271(10)		1.269(6)	
C–O3	1.21(1)	×2	1.289(5)	×2	1.285(4)	×2
Mean	1.250		1.283		1.280	

	Eu(CO ₃)OH	Gd(CO ₃)OH	Tb(CO ₃)OH	Dy(CO ₃)OH	Y(CO ₃)OH	Ho(CO ₃)OH	Er(CO ₃)OH	Tm(CO ₃)OH
RE–O1	2.306(3)	2.300(3)	2.281(3)	2.273(3)	2.247(3)	2.261(4)	2.256(3)	2.232(4)
RE–O1	2.311(3)	2.306(3)	2.283(3)	2.269(3)	2.262(3)	2.262(3)	2.254(3)	2.242(4)
RE–O2	2.499(5)	2.491(6)	2.482(5)	2.463(5)	2.458(5)	2.454(5)	2.442(4)	2.437(5)
RE–O2	2.507(5)	2.497(6)	2.499(5)	2.494(5)	2.490(5)	2.488(5)	2.495(4)	2.490(5)
RE–O4	2.502(5)	2.520(5)	2.478(6)	2.461(6)	2.423(4)	2.428(5)	2.408(4)	2.380(5)
RE–O3	2.548(5)	2.500(6)	2.497(5)	2.479(5)	2.480(4)	2.476(5)	2.477(4)	2.457(5)
RE–O4	2.525(5)	2.520(7)	2.483(4)	2.474(4)	2.440(4)	2.433(5)	2.412(4)	2.400(5)
RE–O3	2.613(5)	2.599(5)	2.599(4)	2.592(4)	2.605(4)	2.602(4)	2.604(4)	2.632(5)
RE–O3	2.682(5)	2.701(6)	2.683(5)	2.667(5)	2.635(4)	2.632(4)	2.620(4)	2.594(5)
RE–O4	2.828(5)	2.813(6)	2.865(5)	2.861(5)	2.939(4)	2.935(4)	2.988(4)	3.018(5)
Mean	2.532	2.525	2.515	2.503	2.498	2.497	2.496	2.488
C–O2	1.264(5)	1.272(5)	1.264(5)	1.273(5)	1.265(6)	1.273(6)	1.260(6)	1.274(7)
C–O3	1.272(8)	1.276(8)	1.285(7)	1.281(6)	1.280(6)	1.273(7)	1.275(6)	1.285(8)
C–O4	1.306(8)	1.285(8)	1.295(7)	1.283(7)	1.289(6)	1.293(7)	1.288(6)	1.288(8)
Mean	1.281	1.278	1.281	1.279	1.278	1.280	1.274	1.282

a: Miyawaki *et al.* (2000)

(O1) bonded to the Tm ions. The crystal structure exhibits a three-dimensional open framework as shown in Fig. 5a. In the crystal structure, the OH and CO₃ groups connect the Tm ions to form a ladder-like structure (Fig. 5b), expressed as the formula $\frac{1}{\infty}[(\text{OH})(\text{CO}_3)\text{RE}_{4/4}]$, which runs parallel to (100) or (010). The ladders are stacked one after another, forming channels with square-cross sections along the *c* axis (Fig. 5c). The Tm ions occupy the connection points of the ladders. While the Tm atom in the orthorhombic phase is nine-coordinated, the Tm atom in this tetragonal phase is eight-coordinated by the oxygen atoms (two from the OH and six from CO₃), forming a dodecahedron (Fig. 6). The eight Tm–O distances range from 2.203(2) to 2.5985(5) Å, which produce a mean distance of 2.364 Å (Table 4). The mean Tm–O distance is shorter than the average of the eight shortest Tm–O distances of the orthorhombic Tm(CO₃)OH, 2.429 Å, confirming that the coordination number of Tm in the tetragonal Tm(CO₃)OH is not nine, but eight. The tetragonal Yb(CO₃)OH is isostructural with the tetragonal Tm(CO₃)OH. The mean Yb–O distance, 2.357 Å, is slightly shorter than the mean Tm–O distance of the tetragonal Tm(CO₃)OH, 2.364 Å, due to the lanthanide contraction (Table 4).

The relationship among the four RE(CO₃)OH structures

Table 6 shows the difference in the RE–CO₃ coordination type among the four RE(CO₃)OH structures. The RE atom is coordinated with ten O atoms from two hydroxyl groups and five carbonate groups in the orthorhombic phase with the kozoite structure. In the 10-coordinated RE-polyhedron, three of the five carbonate groups are coordinated to the RE as chelate ligands, while the other two are coordinated as monodentate ligands. One of the chelate ligands changes to a monodentate ligand with the lanthanide contraction, resulting in a decrease in the coordination numbers from 10 to 9 along with the lowering of the symmetry of structure, from *Pnma* to *P2₁2₁2₁* at RE = Eu.

The crystal structure of the hexagonal Nd(CO₃)OH analyzed by Christensen (1973) contains layers of $\frac{2}{\infty}[(\text{OH})\text{RE}_{3/3}]^{2+}$, in which each hydroxide ion connects three Nd³⁺ ions. The layers are stacked in the [001] direction and are linked by the carbonate groups (Fig. 7). The coordination number of Nd in the hexagonal phase is 9, as is that of Tm in the orthorhombic phase. However, in the hexagonal structure, the RE-polyhedron is coordinated to six oxygen atoms of four carbonate groups, of which two

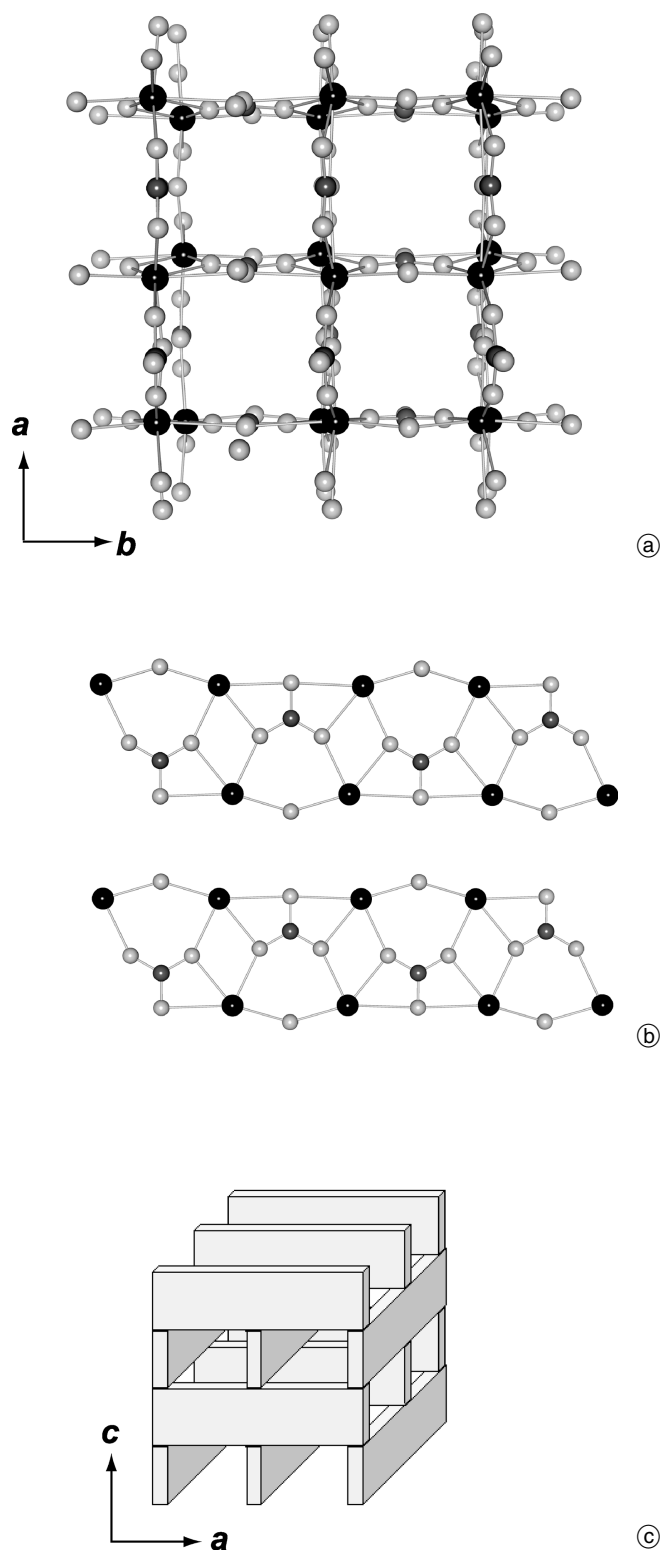


Fig. 5. (a) Projection of the crystal structure of tetragonal $\text{Tm}(\text{CO}_3)\text{OH}$ on (001). Black circles represent Tm atoms, dark grey circles represent C atoms, and light grey circles represent O atoms. (b) Ladder-like structure expressed by the general formula $\frac{1}{\infty}[(\text{OH})(\text{CO}_3)\text{RE}_{4/4}]$ found in the tetragonal phase. (c) A schematic representation of the crystal structure of $\text{Tm}(\text{CO}_3)\text{OH}$. The plate represents the ladder $\frac{1}{\infty}[(\text{OH})(\text{CO}_3)\text{RE}_{4/4}]$.

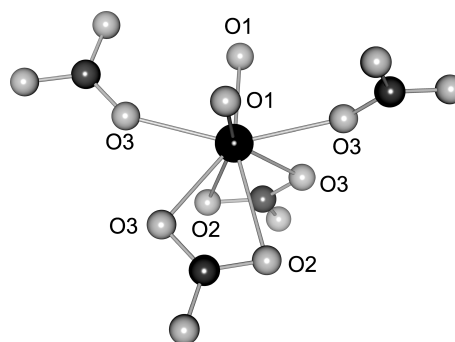


Fig. 6. Drawing of the coordination polyhedron of Tm in tetragonal $\text{Tm}(\text{CO}_3)\text{OH}$.

Table 4. Selected bond length (\AA) for the tetragonal $\text{RE}(\text{CO}_3)\text{OH}$.

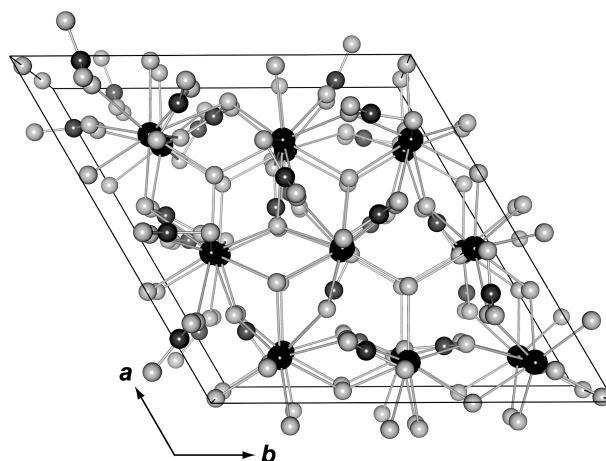
	$\text{Tm}(\text{CO}_3)\text{OH}$		$\text{Yb}(\text{CO}_3)\text{OH}$	
RE–O1	2.203(2)	×2	2.1906(16)	×2
RE–O2	2.5985(5)	×2	2.6021(5)	×2
RE–O3	2.308(4)	×2	2.302(3)	×2
RE–O3	2.348(4)	×2	2.334(3)	×2
Mean	2.364		2.357	
C–O2	1.280(10)		1.281(8)	
C–O3	1.284(6)	×2	1.280(4)	×2
Mean	1.283		1.280	

Table 5. Powder X-ray diffraction data of tetragonal $\text{Tm}(\text{CO}_3)\text{OH}$.

<i>hkl</i>	$\text{Tm}(\text{CO}_3)(\text{OH})$ present study			$\text{Tm}_6(\text{CO}_3)_7(\text{OH})_4$ Kutty <i>et al.</i> (1984)		
	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i> / <i>I</i> ₀	<i>d</i>	<i>I</i> / <i>I</i> ₀	<i>hkl</i>
011	5.97	5.98	6	6.003	30	010
020	4.69	4.70	100	4.701	100	002
021	4.02	4.02	3			
002	3.88	3.88	25	3.874	70	110
121	3.69	3.69	4	3.694	5	012
012	3.58	3.59	1			
220	3.32	3.32	19			
022	2.99	2.99	47	2.987	80	020
031	2.90	2.90	14			
122	2.85	2.85	1			
222	2.52	2.52	36	2.526	70	022
013	2.48	2.49	6			
231	2.47	2.47	21	2.477	80	201
040	2.35	2.35	13			
023	2.27	2.27	2	2.262	10	122
041	2.24	2.25	0			
330	2.22	2.21	1			
123	2.20	2.20	2			
240	2.10	2.10	12	2.102	50	212
042	2.01	2.01	14			
033	1.995	1.994	7			
004	1.940	1.940	9	1.941	50	220
242	1.848	1.847	28	1.850	80	130
233	1.836	1.836	11			
051	1.827	1.826	12	1.831	70	032
341		1.826				

Table 5. (continued)

<i>hkl</i>	Tm(CO ₃)(OH) present study			Tm ₆ (CO ₃) ₇ (OH) ₄ Kutty <i>et al.</i> (1984)		
	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i> / <i>I</i> ₀	<i>d</i>	<i>I</i> / <i>I</i> ₀	<i>hkl</i>
024	1.793	1.793	21	1.794	80	015
043	1.738	1.739	0			
251	1.704	1.702	7	1.706	50	300
224	1.675	1.675	11	1.678	50	301
440	1.662	1.661	4			
350	1.611	1.611	1			
060	1.565	1.566	1	1.562	10	230
442	1.527	1.527	10			
053	1.520	1.520	8			
343		1.520				
044	1.495	1.496	7	1.497	20	040
352	1.486	1.488	2			
260		1.486				
253	1.446	1.446	8			
451	1.441	1.442	6			
244	1.425	1.425	8	1.428	20	042
035	1.390	1.390	3			
235	1.333	1.333	4	1.334	50	206
550		1.329				
071	1.323	1.323	2			
006	1.293	1.293	2			
453		1.276				
271	1.274	1.273	4	1.2755	50	400
444	1.261	1.262	1			
552	1.257	1.257	1			
026	1.246	1.247	5	1.2490	10	332
462	1.236	1.235	2			
370		1.234				
363	1.232	1.232	0			
064	1.218	1.218	1			
226	1.204	1.205	4			
055	1.196	1.197	5			
264	1.179	1.179	2			
255	1.159	1.160	5			
273	1.154	1.155	3			
Tetra. <i>a</i> = 9.396(4) <i>c</i> = 7.759(4) <i>V</i> = 684.48(7)				Ortho. <i>a</i> = 5.118 <i>b</i> = 5.988 <i>c</i> = 9.398 <i>V</i> = 288.02		

**Fig. 7.** Projection of the crystal structure of hexagonal Nd(CO₃)OH onto (001). Black circles represent Nd atoms, dark grey circles represent C atoms, and light grey circles represent O atoms.

are chelate ligands and the other two are monodentate ligands. The other three oxygen atoms are from the three hydroxyl groups. It is worth noting that the hexagonal and orthorhombic phases are the more or less dense phases of RE(CO₃)(OH), respectively (see density in Table 6). The present synthetic study has shown that hexagonal Nd(CO₃)(OH) was obtained by reaction at 220 °C and pressure of 500 kg/cm², while the orthorhombic phase was obtained by reaction at 220 °C and pressure of 50 kg/cm² indicating that the hexagonal and orthorhombic phases are the high- and low-pressure phases of Nd(CO₃)(OH), respectively.

The rare earth atom in the tetragonal structure is coordinated by eight O atoms. This is the smallest coordination number for the rare earth atoms among the four RE(CO₃)OH structures. In the tetragonal structure, the RE-polyhedron is coordinated to six oxygen atoms of four carbonate groups, of which two are chelate ligands and the other two are monodentate ligands, similar to the RE-polyhedron in the hexagonal structure (Fig. 8). The number of hydroxyl groups coordinating to the RE-polyhedron in the tetragonal structure is two, while it is three in the hexagonal phase (Table 6). Consequently, the RE-polyhedron in the tetragonal phase has the lower coordination number of 8.

Despite the similarity in the coordination type between the tetragonal and hexagonal phases, the crystal structure of the hexagonal phase cannot be derived from that of the tetragonal phase, as is found in the structural relationship between the two types of orthorhombic phases. The remark-

Table 6. Coordination type of RE-O in RE(CO₃)OH.

Phase	C.N.	Space group	No. of ions coordinating to RE		Density (g/cm ³)
			Carbonate (chelate, monodentate)	Hydroxyl	
Hexagonal (Nd) ^a (hydroxyl bastanäsité structure)	9	<i>P</i> $\bar{6}$	4 (2, 2)	3	5.09
Orthorhombic (Nd) (Kozoite structure)	10	<i>Pnma</i>	5 (3, 2)	2	4.820
Orthorhombic (Tm)	9	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁	5 (2, 3)	2	5.801
Tetragonal (Tm)	8	<i>P4</i> ₂ / <i>nmc</i>	4 (2, 2)	2	4.773

a: Christensen (1973)

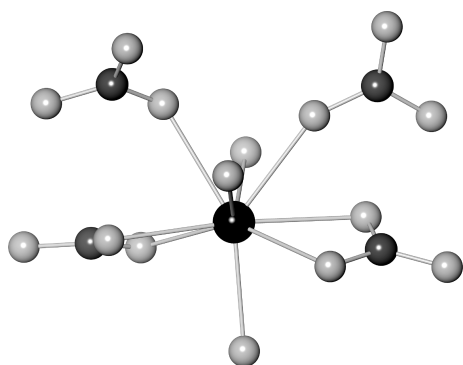


Fig. 8. Drawing of the coordination polyhedron of Nd in hexagonal $\text{Nd}(\text{CO}_3)\text{OH}$. Black circles represent Nd atoms, dark grey circles represent C atoms, and light grey circles represent O atoms.

able difference in the coordination type between the tetragonal and hexagonal phases is the number of hydroxyl groups. It is impossible for the hydroxyl groups to be consecutively expelled from the first coordination sphere with the lanthanide contraction, because the RE–OH bonds are stronger and their bond lengths are shorter than the RE–CO₃ bonds. Therefore, no consecutive transformation from a hexagonal to a tetragonal structure can be expected with the lanthanide contraction.

In conclusion, the present study has provided us with a comprehensive view of the crystal structures of the RE(CO₃)OH type phases, resulting in a better understanding of the structural relationships of complex rare earth carbonate minerals, including kozoite, bastnäsite, ancylite, etc.

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