

Crystal Structure and Phase Transitions of $\text{Gd}(\text{CO}_3)\text{OH}$ Studied by Synchrotron Powder Diffraction

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The crystal structure of $\text{Gd}(\text{CO}_3)\text{OH}$ was solved using synchrotron powder X-ray diffraction. $\text{Gd}(\text{CO}_3)\text{OH}$ was known to exist in a form $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ and its powder pattern has been listed in JCPDF (#430604) for decades, but the crystal structure has not yet been elucidated. The crystal structure is solved with simulated annealing and the DASH program. The final Rietveld refinement converged to $R_w = 6.28\%$, $R_p = 4.47\%$ and $\chi^2 = 1.348$, using the GSAS program. $\text{Gd}(\text{CO}_3)\text{OH}$ crystallizes in orthorhombic system with lattice parameters $a = 7.08109(9)$, $b = 4.88436(7)$, $c = 8.45010(13)$ Å and space group $Pnma$. $\text{Gd}(\text{CO}_3)\text{OH}$ forms a three-dimensional framework with an eight-membered ring, a one-dimensional channel and OH^- in the cavity. XANES of Gd L_{III} -edge indicates that the oxidation state of Gd is 3+. Two phase transitions of $\text{Gd}(\text{CO}_3)\text{OH}$ were found at 500 and 650 °C to yield $\text{Gd}_2\text{O}_3\text{CO}_3$ and Gd_2O_3 respectively.

Keywords: Rare-earth compound; Crystal structure; *In-situ* powder diffraction; Phase transition.

INTRODUCTION

Gd compounds have attracted much attention because of their prospective applications, for example, in phosphor materials for large flat display panels^{1,2} and as a contrast agent for magnetic-resonance imaging (MRI) in the sciences.^{3,4} Biocompatible amorphous $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ has been demonstrated to enhance T_1 and to decrease T_2 in nuclear magnetic resonance effects, and thus is an alternative MRI contrast agent. $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ with appropriate surface modifications is an ideal template for the formation of hollow SiO_2 nanoshells and hollow $\text{SiO}_2\text{-Fe}_3\text{O}_4$ hybrid composites. $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ has prospects for the development of innovative composite materials and multifunctional biomaterials with imaging, targeting, delivery and therapeutic capabilities.⁵

Although $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ has been known for decades, and its powder diffraction pattern has been listed in JCPDF since 1987,⁷ its crystal structure has remained undetermined. The crystal system and unit cell parameters are unassigned in JCPDF. Werner attributed the diffraction pattern to hexagonal cells ($a = 9.744$, $c = 7.063$ Å, $V = 580.8$ Å³) with possible geometric ambiguity associated with

orthorhombic cells ($a = 7.070$, $b = 8.435$, $c = 4.878$ Å, $V = 290$ Å³).⁸ The hexagonal and orthorhombic cells are geometrically related, with $b/c \approx \sqrt{3}$.

$\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ has great thermal stability, as revealed by thermogravimetric analysis.^{2,6,9} Its decomposition temperature is as high as ~500 °C. Park *et al.*² suggested that the first intense endothermic feature of $\text{Gd}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ at 497 °C might be associated with the simultaneous dehydration and decomposition of carbonate groups. Dehydration rarely occurs at such a high temperature. A detailed crystalline structure might provide useful information about this anomalous effect.

We have already described a possible crystal system, of hexagonal cells.⁶ As no sufficiently large single crystal is available, our objective in this investigation was to solve the crystal structure from powder diffraction data. We discuss the great thermal stability associated with water of crystallization or the OH^- anion in the Gd compound. The oxidation state of Gd was examined with X-ray absorption near-edge spectra. *In-situ* X-ray powder diffraction was employed to define the phase transitions of $\text{Gd}(\text{CO}_3)\text{OH}$; two occurred at ~500 °C and 650 °C, which we assign to

Dedicated to Professor Ho-Utsiang Wei on the occasion of his 70th birthday.

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$\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 crystalline phases, respectively. We applied Rietveld refinement to solve the crystal structures for $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 .

EXPERIMENTS

The synthesis of $\text{Gd}(\text{CO}_3)\text{OH}$ was followed the procedure in literature.⁶ For the spherical and rhombus-like particles, the typical preparation was performed by the addition of urea (1 mmol, 99 %, Alfa Aesar) and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.25 mmol, 99.5 %, Aldrich) to distilled water (10 ml) with constant stirring for 10 min. After fully dissolved, the transparent solutions were maintained at $\sim 90^\circ\text{C}$ for a period of 4 (spheres) or 10 h (rhombus), leading to the formation of white precipitates. The white precipitates were then collected by centrifugation and washed three times with distilled water. This was followed by evaporation of the solvent in a vacuum desiccator. The rice-shaped mixtures were obtained from a [urea]/[$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$] ratio of 8 for a reaction of 10 h at $\sim 90^\circ\text{C}$.

The powder X-ray diffraction pattern of $\text{Gd}(\text{CO}_3)\text{OH}$ particles was recorded at the BL01C2 beamline of National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The ring of NSRRC was operated at energy 1.5 GeV with a typical current 300 mA. The wavelength of the incident X-rays was $0.9537 \text{ \AA}$ (13.0 keV), delivered from the superconducting wavelength-shifting magnet and a Si(111) double-crystal monochromator. The diffraction pattern was recorded with a Mar345 imaging plate detector approximately 300 mm from the sample and typical exposure duration 5 min. The pixel size of Mar345 was $100 \text{ }\mu\text{m}$. The one-dimensional powder diffraction profile was converted with program FIT2D and cake-type integration. The diffraction angles were calibrated according to Bragg positions of Ag-Benhenate and Si powder (NBS640b) standards. *In situ* synchrotron X-ray powder diffraction for $\text{Gd}(\text{CO}_3)\text{OH}$ was performed at BL01C2 from 23°C to 650°C with a heating rate approximately $4^\circ\text{C}/\text{min}$. The powder sample was sealed in a quartz capillary (0.5 mm diameter) and heated in a stream of hot air; each *in-situ* powder XRD pattern was exposed for about 1 min.

The structure was determined from the powder diffraction data with program DASH.¹⁶ Powder diffraction data were indexed with DievoI and Treor. The structure factors of the powder diffraction patterns were extracted with Pawley's method, and simulated annealing was employed to determine the crystal structure. The final refinement with the Rietveld method was performed with the

GSAS program.²¹

X-ray absorption near edge spectra (XANES) of the Gd L_{III} -edge was performed at NSRRC beamline BL17C1, using a Si (111) double-crystal monochromator and a focusing mirror to focus X-ray beam and suppress higher harmonics. The ground powder sample was attached to Scotch tape. XANES was conducted in a transmission mode before and behind the sample with two ionization chambers filled with gaseous N_2 . The Gd L_{III} -edge spectrum was scanned from 7000 to 7900 eV in steps 0.3 eV close to the near edge and 1-2 eV above the edge.

RESULTS AND DISCUSSION

$\text{GdO}(\text{CO}_3)\text{OH}$ particles were synthesized on refluxing aqueous solutions of gadolinium salt and urea. The duration of reaction and ratio of concentrations of [urea] to [$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$] were controlled to yield three polymorphous: spherical, rhombus and rice-shaped nanoparticles. Park *et al.* elucidated the effects of the concentration of urea and the reaction temperature on the morphology of Gd compounds too.² The spherical particles have an average diameter of $478 \pm 70.8 \text{ nm}$ estimated by SEM.⁶ The rhombus-shaped particles displayed an average size of 471.2 nm in height and 198.9 nm in diameter. The rice-shaped particles have an average length of $585.1 \pm 143.0 \text{ nm}$ and diameter of $2 \times 4.7 + 53.0 \text{ nm}$. Fig. 1 presents the powder X-ray diffraction patterns of the spheres and rhombus particles. The spheres yielded a dominant amorphous signal and some tiny diffraction features. The rhombus- and rice-

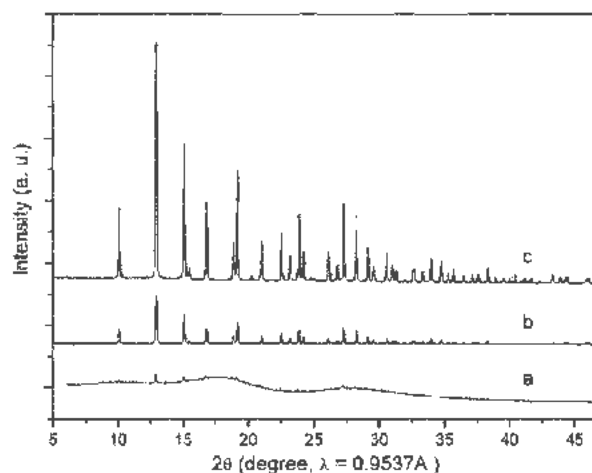


Fig. 1. Synchrotron powder X-ray diffraction patterns of $\text{Gd}(\text{CO}_3)\text{OH}$ (a) sphere (b) sphere ($\times 10$) subtracted background (c) rhombus particles.

shaped particles yielded similar diffraction patterns. The tiny features from the sphere particles (Fig. 1b) occurred at diffraction angles similar to those from the rhombus particles (Fig. 1c). These XRD patterns indicate that the three samples contained the same crystalline phase. The grain size of rhombus-shaped particles was estimated with Scherrer's equation to be 46.8 nm.

Powder diffraction data were indexed using programs Diovol and Treor. Both programs revealed that the best fitting unit cell was hexagonal. In a reasonable crystal model, the Gd compound contained a carbonate, H_2O and GdO_x polyhedron; all attempts to find a practical model to fit such a highly symmetric crystal system eventually failed. The crystal phase also was indeterminate by direct method. After substantial difficulty, we decided to reduce the symmetry to that of orthorhombic crystal system. The structure factors were extracted with Pawley's method. We undertook simulated annealing to solve the crystal structure using the DASH program. With the GSAS program, the final refinement with the Rietveld method (Fig. 2) converged to $R_{\text{wp}} = 6.28\%$, $R_p = 4.47\%$ and $\chi^2 = 1.348$. The crystal data of $\text{Gd}(\text{CO}_3)\text{OH}$ are listed in Table 1, atomic coordinates in Table 2 and selected interatomic distances and bond angles in Table 3. All atomic positions and thermal parameters are adjusted in the Rietveld refinement, except that the position of the H atom was set according to its theoretical position with occupancy 0.5. The mean distance between Gd and O of carbonate is 2.5 ~ 2.7 Å. The distance between Gd and OH an-

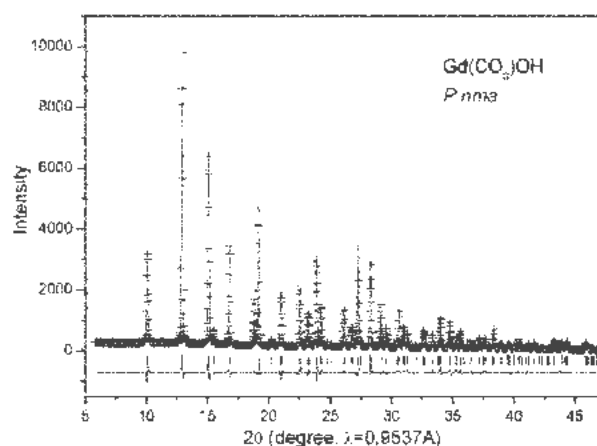


Fig. 2. Rietveld refinement of $\text{Gd}(\text{CO}_3)\text{OH}$. (○): experimental data; solid line: simulation curve; short tick: Bragg diffraction position; lower curve: difference between experimental and simulated data.

Table 1. Crystal data for $\text{Gd}(\text{CO}_3)\text{OH}$, $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3

formula	$\text{Gd}(\text{CO}_3)\text{OH}$	$\text{Gd}_2\text{O}_2\text{CO}_3$	Gd_2O_3
mass/g	234.25	406.5	362.5
wavelength/Å	0.9537	0.9537	0.9537
temperature/ $^{\circ}\text{C}$	25	545	650
space group	$Pnma$	$P6_3/mmc$	$Ia-3$
cell parameters/Å	$a = 7.08109(9)$, $b = 4.88436(7)$, $c = 8.45010(13)$	$a = 3.9222(1)$, $a = 10.8906(1)$	
cell volume/Å ³	292.26	205.99	1291.68
Z	4	2	16
$D_{\text{calc}}/\text{Mg/m}^3$	3.21	3.95	4.49
$R_{\text{wp}}/\%$	6.28	2.62	3.65
$R_p/\%$	4.47	1.77	2.41
χ^2	1.348	1.435	0.86
grain size /nm	46.8	20.0	25.7

Table 2. Fractional atomic coordinates and thermal parameters for $\text{Gd}(\text{CO}_3)\text{OH}$, $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3

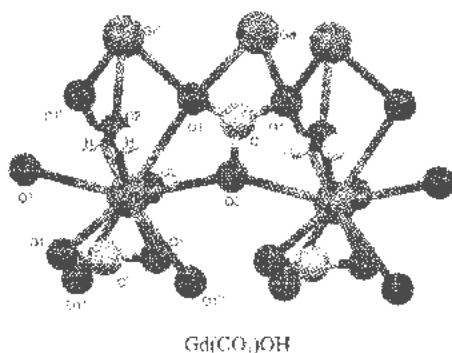
	X	Y	Z	$U_{\text{iso}} \times 100$
Name: $\text{Gd}(\text{CO}_3)\text{OH}$				
Gd1	0.3594(2)	0.25	0.8352(2)	5.99(5)
O1	0.157(1)	-0.023(2)	0.6126(9)	8.2(3)
O2	0.037(1)	0.25	0.889(1)	6.6(4)
O3	0.295(2)	-0.25	0.799(2)	9.1(5)
C1	0.197(4)	-0.25	0.663(5)	14.0(9)
H1	-0.0026	0.147	0.976	17.0
Gd2				
Name: $\text{Gd}_2\text{O}_2\text{CO}_3$				
Gd1	1/3	2/3	0.09410(7)	3.78(4)
O1	0.260(3)	0.520(5)	1/4	8.8(3)
O2	0	0	0.1759(9)	8.8(3)
O3	1/3	2/3	0.5558(5)	8.8(3)
C1	0.05(2)	0.09(3)	1/4	13.(3)
H1				
Gd2				
Name: Gd_2O_3				
Gd1	1/4	1/4	1/2	3.5(1)
O1	0.3904(9)	0.1513(9)	0.379(1)	2.0(2)
O2				
O3				
C1				
H1				
Gd2	0.9710(1)	0	1/2	3.73(6)

ion is only ~2.3 Å. Fig. 3 indicates that $\text{Gd}(\text{CO}_3)\text{OH}$ formed a three-dimensional framework structure, assembled from a GdO_{10} polyhedron, with CO_3^{2-} and OH^- anion groups. The Gd atom is coordinated with ten oxygen atoms, eight from CO_3^{2-} groups and two from OH^- anions; the C atom is coordinated with three O atoms to form a carbonate. A fragment of $\text{Gd}(\text{CO}_3)\text{OH}$ is shown below with atomic names labeled.

Table 3. Selected interatomic distances and bond angles for $\text{Gd}(\text{CO}_3)\text{OH}$, $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3

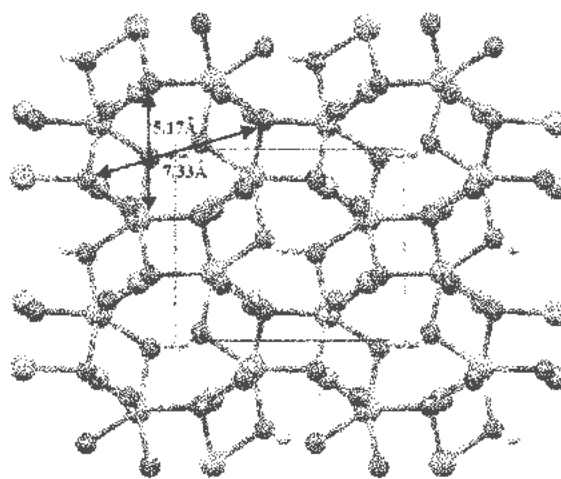
Compounds	interatomic distance / Å			bond angle / deg		
	GdCO_3OH	$\text{Gd}_2\text{O}_2\text{CO}_3$	Gd_2O_3	GdCO_3OH	$\text{Gd}_2\text{O}_2\text{CO}_3$	Gd_2O_3
Gd–Gd ⁱ	3.8222(9)	3.9222(1)	3.6340(8)	O1–Gd–O1 ⁱ	58.82(2)	72.6(2)
Gd–O1	2.716(7)	2.462(4)	2.416(9)	O1–Gd–O2	67.44(3)	67.1(3)
Gd–O1 ⁱ	2.595(7)	2.462(4)		O1–Gd–O3	48.73(3)	98.6(3)
Gd–O1 ⁱⁱⁱ	2.532(7)	2.462(4)		O2–Gd–O3	81.04(3)	119.2(3)
Gd–O2	2.330(8)	2.594(6)		O2–Gd–O1 ⁱ	81.04(2)	75.4(2)
Gd–O2 ⁱ	2.270(9)	2.594(6)	2.29(1)	O1–C–O1 ⁱⁱ	130.44(5)	149.0(10)
Gd–O3	2.503(3)	2.341(2)	2.34(2)	O1–C–O3	114.75(5)	106.0(5)
C–O1	1.221(3)	1.19(4)				
C–O3	1.344(3)	1.45(12)				

Gd, O2, O3 and C were located on mirror planes. When the OH^- anion is ignored, the Gd compound forms an eight-membered ring framework and a one-dimensional channel along the b axis with hole dimensions 5.17×7.33 Å. The framework of $\text{Gd}(\text{CO}_3)\text{OH}$ resembles that of $[\text{Y}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)(\text{CO}_3)_2$ ¹² but with OH^- in the cavity. $[\text{Y}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)(\text{CO}_3)_2$ is also assembled from YO_6 polyhedron, carbonate, H_2O , and a C_2O_4 group forming a one-dimensional network along the a axis. The channel size of $[\text{Y}(\text{H}_2\text{O})]_2(\text{C}_2\text{O}_4)(\text{CO}_3)_2$ is 4.7×6.2 Å. $\text{Gd}(\text{CO}_3)\text{OH}$ potentially serves as a porous material in some applications, such as hydrogen storage or secondary lithium-ion batteries.



Whether a Gd compound contains H_2O or OH^- anions is difficult to determine with X-ray diffraction because of the small scattering power of H atoms. H_2O is electrically neutral whereas the OH^- anion is negatively charged; the oxidation state of Gd would be +2 if the compound contains H_2O and +3 if it contains OH^- anions. For that reason we applied Gd L_{III} -edge XANES to determine the oxidation states of Gd compounds. Hess *et al.*¹³ established that Gd L_{III} -edge spectra can be used to elucidate the structural phase transition in $\text{Gd}_2(\text{Ti}, \text{Zr})_2\text{O}_7$ pyrochlores. Imaki *et al.*¹² investigated with X-ray absorption spectra the electro-

chemical behavior of the perovskite, $\text{Gd}_{1-x}\text{TaO}_3$, with deficient A-site, and the variation of its electronic structure upon insertion of lithium. Gd L_{III} -edge and Ta L_I -edge XAS revealed that, during the electrochemical insertion of lithium, the Gd ion made no contribution to charge compensation, but the Ta ion was reduced. We applied XANES to the Gd L_{III} -edge of $\text{Gd}(\text{CO}_3)\text{OH}$ to assess the oxidation state of Gd. Fig. 4 displays XANES of Gd L_{III} -edge of $\text{Gd}(\text{CO}_3)\text{OH}$ (rhombus) and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$. The X-ray absorption edge of $\text{Gd}(\text{CO}_3)\text{OH}$ is the same as that in $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$. The X-ray absorption edge energies, E_0 , are 7239.5 and 7239.0 eV for $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{CO}_3)\text{OH}$ particles respectively. E_0 represents the edge energy of the X-ray absorption spectra, obtained from the first point of inflection near the absorption edge. The XANES results reveal that the oxidation state of Gd was 3+ in all these samples. Accordingly, the linkage group in the Gd-complex is an OH^- anion rather than a H_2O group. In summary, we suggest $\text{Gd}(\text{CO}_3)\text{OH}$ to

Fig. 3. Crystal packing for $\text{Gd}(\text{CO}_3)\text{OH}$ along the b axis.

be the most appropriate formula of the Gd compound.

Gd(CO₃)OH is one member of a family of rare-earth hydroxycarbonates [Ln(CO₃)OH] that have been exten-

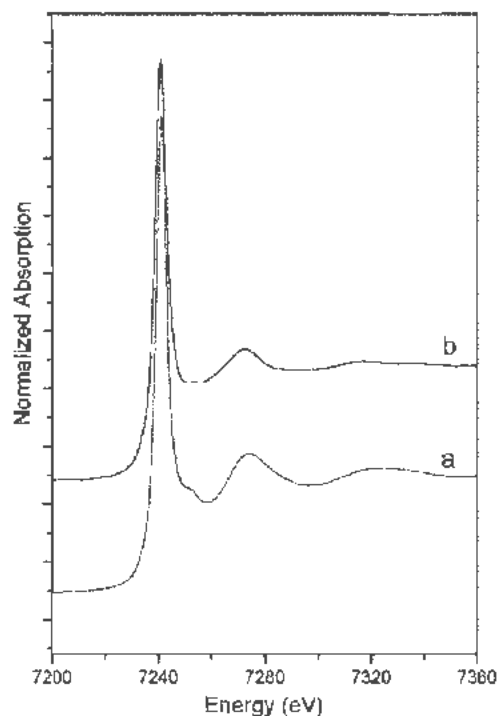


Fig. 4. XANES spectrum for Gd L_{III}-edge for (a) GdCl₃·6H₂O (b) Gd(CO₃)OH.

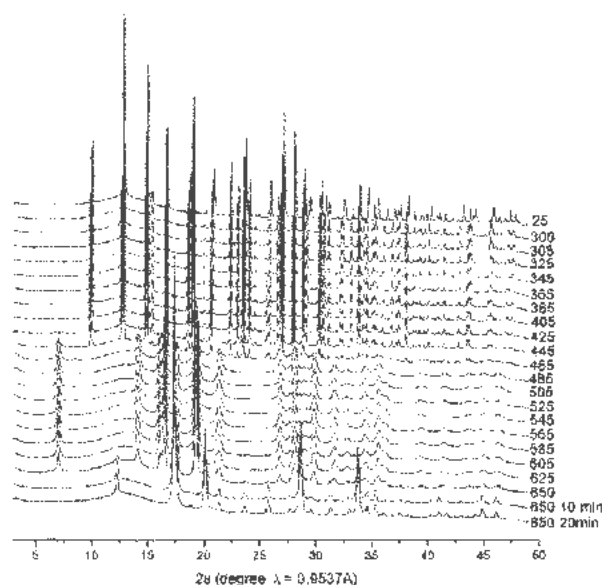


Fig. 5. *In-situ* synchrotron X-ray powder diffraction, 25–650 °C, for rhombus-shaped Gd(CO₃)OH.

sively studied.^{15–24} Caro *et al.* asserted the existence of two forms of Ln(CO₃)OH: A-type (ancylite), Ln(OH)CO₃, is orthorhombic and B-type (nastnaesite) is hexagonal.¹⁷ The OH infrared absorptions in both types are narrow, revealing a narrow distribution of states of vibrational energy. The chemical environment of the OH[−] group is simple. Xu and Feng *et al.* determined the structures of Sm(CO₃)OH²⁰ and Nd(CO₃)OH²¹ with single-crystal diffraction. Our results suggest that the crystal structure of Gd(CO₃)OH is isomorphous with those of Sm(CO₃)OH and Nd(CO₃)OH.

Our thermogravimetric analysis (TGA) of Gd(CO₃)OH⁶ showed that the first stage of loss of mass occurs at ~500 °C for the rhombus sample, indicating the Gd-complex to be thermally stable. Park *et al.* found that a large loss of mass of Gd₂O(CO₃)₂·H₂O to occur at 497 °C,² and suggested that this phenomenon was associated with a simultaneous dehydration and decomposition of carbonate groups, as in the case of Nd₂O(CO₃)₂·1.5H₂O.¹⁷ Our information on the crystalline structure demonstrates that a superior description of this Gd compound would involve the OH[−] anion rather than water; this OH[−] anion is bound between two Gd atoms. The noticeably small interatomic distance Gd–O(H), ~2.3 Å, corresponds to strong binding, which is responsible for a tight link between OH[−] anions and the Gd framework, thus perhaps explaining that Gd(CO₃)OH has such great thermal stability.

Fig. 5 exhibits the *in-situ* X-ray powder diffraction for rhombus Gd(CO₃)OH from 23 °C to 650 °C. Two phases transition were observed. The first phase transition occurred at ~500 °C and was complete at ~510 °C, which is consistent with TGA analysis for the first loss of mass at a similar temperature. We assign the crystalline phase above 500 °C to be Gd₂O₂CO₃ according to JCPDS. When the sample was heated to 650 °C a second phase appeared. We maintained the sample at 650 °C for 20 min for the phase transition to complete. This second phase is assigned to Gd₂O₃ according to the JCPDS file.

Gd₂O₂CO₃ crystallizes in a hexagonal crystal system although its crystal structure has not been determined. Christensen¹⁵ and Attfield and Ferey²⁶ mentioned that synchrotron and conventional XRD patterns for Nd₂O₂CO₃ and La₂O₂CO₃ were completely indexed on the hexagonal unit cells. Olafsen *et al.* solved the crystal structures of Ln₂O₂CO₃ (Ln = La and Nd) with high-resolution powder neutron (PND) and synchrotron X-ray diffraction (SXRD) combined with selected-area electron diffraction (SAED).²⁷ Olafsen demonstrated that SXRD of La₂O₂CO₃ exhibits

an average structure of hexagonal symmetry with disorder of the CO_3 group (one C and one O atoms were disordered in the hexagonal crystal structure). PND patterns showed satellite features associated with a modulated structure from the carbonate group. Electron diffraction (SAED) demonstrated clear single-crystal diffraction patterns of modulated structures of $\text{La}_2\text{O}_2\text{CO}_3$; Olafsen *et al* thus refined the PND patterns with orthorhombic, $Ama2$, and monoclinic, $C2/c$, crystal systems for $\text{La}_2\text{O}_2\text{CO}_3$. Two-dimensional modulated structures were employed to describe the $\text{La}_2\text{O}_2\text{CO}_3$ crystal structures. We used hexagonal symmetry with space group $P6_3/mmc$ to refine our synchrotron XRD pattern of $\text{Gd}_2\text{O}_2\text{CO}_3$ with the Rietveld method. A $\text{Gd}_2\text{O}_2\text{CO}_3$ XRD pattern at $\sim 545^\circ\text{C}$ was selected for Rietveld refinement. The atomic coordinates of $\text{La}_2\text{O}_2\text{CO}_3$ in hexagonal symmetry were chosen from the literature³⁷ for an initial model. Fig. 6 displays the Rietveld refined patterns for $\text{Gd}_2\text{O}_2\text{CO}_3$ at $\sim 545^\circ\text{C}$. The crystal data of $\text{Gd}_2\text{O}_2\text{CO}_3$ are listed in Table 1, atomic coordinates in Table 2 and selected interatomic distances and bond angles in Table 3. $\text{Gd}_2\text{O}_2\text{CO}_3$ is considered to be two $\text{Gd}(\text{CO}_3)\text{OH}$ and one lost H_2CO_3 . Compounds lost during thermal decomposition might be H_2O and CO_2 , consistent with previous reports^{2,15} predicting a loss of mass at $\sim 500^\circ\text{C}$ to be associated with dehydration and decomposition of carbonate. A slight modification is that H_2O might come from the rearrangement and decomposition of two OH groups. The $\text{Gd}_2\text{O}_2\text{CO}_3$ crystal structure contains no one-dimensional channel structure but crystallizes with alternating $(\text{Gd}_2\text{O}_2)_n$

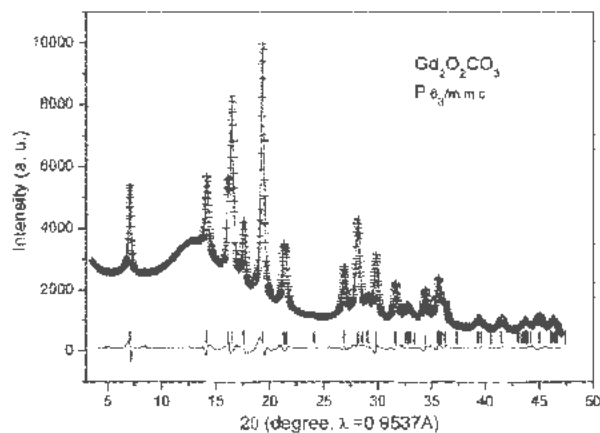


Fig. 6. Rietveld refinement of $\text{Gd}_2\text{O}_2\text{CO}_3$ at 545°C . (—): experimental data; solid line: simulation curve; short tick: Bragg diffraction position; lower curve: difference between experimental and simulated data

and carbonate layers along the c axis for layer distances 5.45 and 2.29 Å respectively (Fig. 7). In $\text{Gd}_2\text{O}_2\text{CO}_3$, Gd is coordinated with eight O atoms to form a GdO_8 polyhedron. The average Gd–O distance is 2.45 Å, shorter than that in $\text{Gd}(\text{CO}_3)\text{OH}$, ~ 2.6 Å. The calculated crystal densities are 3.21 and 3.95 Mg/m^3 for $\text{Gd}(\text{CO}_3)\text{OH}$ and $\text{Gd}_2\text{O}_2\text{CO}_3$ respectively, which indicate that, with H_2CO_3 decomposition, $\text{Gd}_2\text{O}_2\text{CO}_3$ becomes denser than $\text{Gd}(\text{CO}_3)\text{OH}$.

With increasing temperature we saw a succession of phase transitions. $\text{Gd}_2\text{O}_2\text{CO}_3$ turned to Gd_2O_3 near 650°C . The phase transition became completed when the sample was maintained at 650°C for 20 min. $\text{Gd}_2\text{O}_2\text{CO}_3$ lost one CO_2 group during thermal decomposition. Gd_2O_3 crystallizes in a cubic system with space group $Ia\bar{3}$.^{38,39} Fig. 8 shows the Rietveld refinement for powder XRD pattern of Gd_2O_3 at 650°C . The crystal data of Gd_2O_3 are listed in Table 1, atomic coordinates in Table 2 and selected interatomic distances and bond angles in Table 3. No disorder or modulated structure was found in Gd_2O_3 . Gd in Gd_2O_3 is coordinated with six O atoms to form an octahedral structure. The average Gd–O bond distance is ~ 2.35 Å, shorter than in

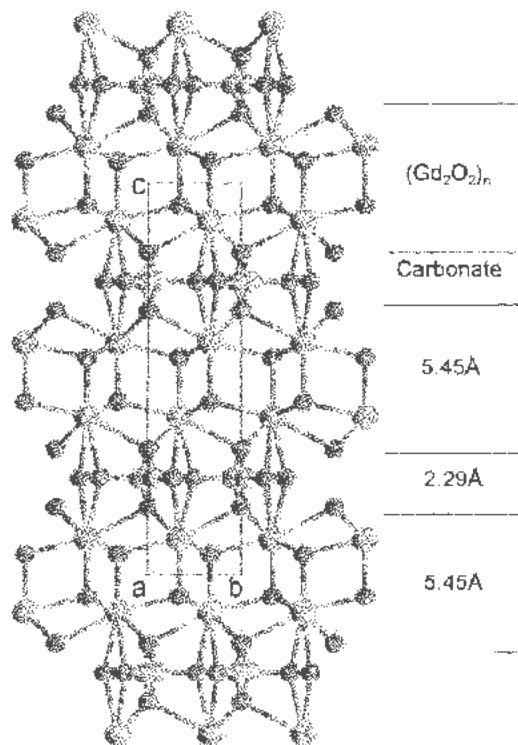


Fig. 7. Crystal packing of $\text{Gd}_2\text{O}_2\text{CO}_3$ in which $(\text{Gd}_2\text{O}_2)_n$ and carbonate groups form a layer structure along the c axis.

$\text{Gd}_2\text{O}_2\text{CO}_3$ and $\text{Gd}_2(\text{CO}_3)\text{OH}$. The calculated density for Gd_2O_3 is 4.49 Mg/m^3 which is much greater than in $\text{Gd}_2\text{O}_2\text{CO}_3$ and $\text{Gd}_2(\text{CO}_3)\text{OH}$. Because of the great chemical and thermal stability at high temperatures, Gd_2O_3 and its derivatives have been investigated for diverse applications, including high-efficiency phosphors,^{30,31} ferroelectric memory,³² and optical detection and visualization of antibody patterns.³²

CONCLUSION

The crystal structure of $\text{Gd}(\text{CO}_3)\text{OH}$ was determined by synchrotron X-ray powder diffraction. $\text{Gd}(\text{CO}_3)\text{OH}$ has a three-dimensional network with Gd coordinated with carbonate and OH^- anion groups. A strong link between Gd and OH^- endows it with great thermal stability. XANES of the Gd $L_{2,3}$ -edge of $\text{Gd}(\text{CO}_3)\text{OH}$ revealed that the oxidation state of Gd is +3. *In-situ* Powder X-ray diffractometry was applied to study the phase transition of $\text{Gd}(\text{CO}_3)\text{OH}$. Two crystalline phases were found at ~ 500 and 650°C and assigned to $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 , respectively. The detailed crystal structures of $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 were obtained on Rietveld refinement. The Gd coordination number decreased from 10 and 8 to 6 for $\text{Gd}(\text{CO}_3)\text{OH}$, $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 , respectively, following the phase transitions. The Gd–O distances in $\text{Gd}(\text{CO}_3)\text{OH}$, $\text{Gd}_2\text{O}_2\text{CO}_3$ and Gd_2O_3 decreased following the phase transitions, so that these Gd compounds became denser.

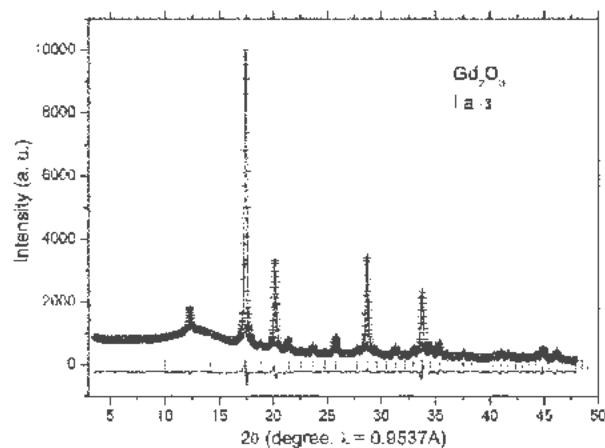


Fig. 8. Rietveld refinement of Gd_2O_3 at 650°C . (+): experimental data; solid line: simulation curve; short tick: Bragg diffraction position; lower curve: difference between experimental and simulated data.

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Supplementary Material

The supplementary crystallographic information file (CIF) for $\text{Gd}(\text{CO}_3)\text{OH}$ can be obtained free of charge via the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany. (Fax: +49 7247 808 666; E-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-number 421595.

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