Refinement of the crystal structure of gallium oxide hydroxide, GaO(OH)

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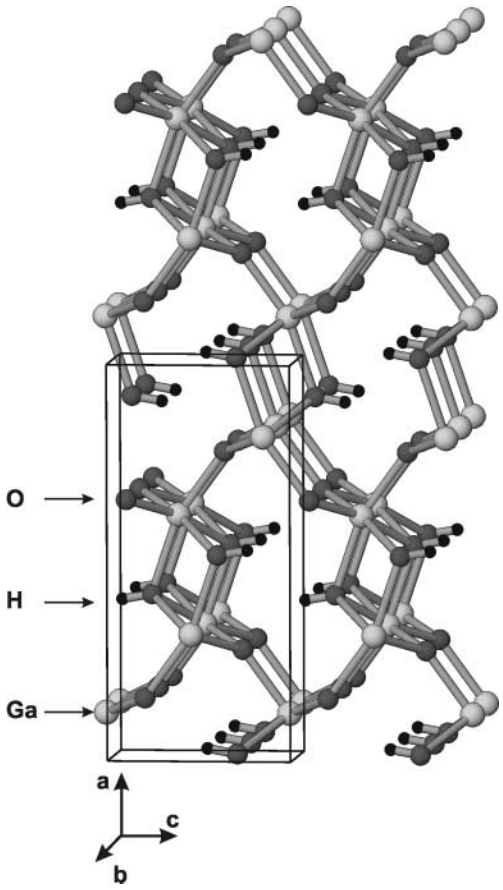

Abstract

$GaHO_2$, orthorhombic, *Pnma* (No. 62), $a = 9.7907(8)$ Å, $b = 2.9732(2)$ Å, $c = 4.5171(4)$ Å, $V = 131.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0403$, $wR_{ref}(F^2) = 0.081$, $T = 293$ K.

Source of material

The title compound was one of several phases synthesized by a hydrothermal reaction of metal gallium, $CdCl_2$, iodine, DMF and ammonia in sealed teflon-lined stainless steel autoclave at 448 K for 2 days. Transparent prism-like crystals were recovered by filtration.

Discussion

Gallium oxide hydroxide GaO(OH), also known as gallium oxyhydroxide, oxyhydrate or monohydrate with the diaspore structure [1-2], is widely used to synthesize various gallophosphates, a new family of three-dimensional open-framework microporous materials. These materials have attracted intense interest due to their industrial applications in catalysis, sorption, ion-exchange processes, and gas separation [3-8]. GaO(OH) can also be used to produce ceramics such as $ZnGa_2O_4$ and $LaGaO_3$ [9] for luminescent phosphor application in vacuum fluorescent or field emission displays. It has also been employed with HBr as a novel chemical wet etchant for the fabrication of 1-D laser waveguides [10]. There are several approaches to prepare gallium oxide hydroxide: by heating either α-Ga_2O_3 or δ-Ga_2O_3 in wet atmosphere [11], by heating gallium metal with water in an autoclave at 200 °C, by dehydration of gallium trihydroxide at 100 °C, or by hydrolysis of gallium salts (e.g. chloride, nitrate, and perchlorate) [12]. In addition, sonochemical reaction can yield excellent scroll-like cylindrical GaO(OH) nanoparticles [13].

To date, two different crystal structures have been reported for the title compound. The deuteriohydroxide, GaO(OD), crystallizes in the space group *Pbnm* ($a = 4.516$ Å, $b = 9.779$ Å, $c = 2.966$ Å), as determined by a profile analysis of powder neutron diffraction data [11]. Another one belongs to the space group *Fddd* ($a = 10.140$ Å, $b = 8.321$ Å, $c = 7.010$ Å) [14]. This leads to the speculation that deuterium and hydrogen would make the difference in the structure. In this report, we present a refinement of the oxide hydroxide compound.

The refinement shows that the oxide hydroxide has the same structure as that of the oxide deuteriohydroxide. During the refinement, the hydrogen position could be located via the difference map of electron density. The hydrogen atom is attached to O2, which is bonded to three Ga atoms at distances 2.054 Å, 2.054 Å and 2.055 Å. This is to be compared to O1, which is also bonded to three Ga atoms, but at distances 1.929 Å, 1.929 Å and 1.934 Å. The bonding geometry around O1 is more flat, as the three O1—Ga bonds make angles of 100.8°, 123.4° and 123.4°. The bonding geometry around O2 is more puckered, and the three O2—Ga bonds have angles of 92.7°, 103.7° and 103.7°.

Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.02 × 0.02 × 0.02 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	202.77 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	61.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1466, 234
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 233
$N(param)_{refined}$:	23
Programs:	SHELXL-97 [15], SADABS [16]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*c*	0.43(2)	3/4	0.14(4)	0.05(6)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga	4*c*	0.35544(9)	1/4	0.5517(2)	0.0041(5)	0.0041(5)	0.0057(5)	0	0.0004(4)	0
O(1)	4*c*	0.1953(6)	1/4	0.301(1)	0.006(3)	0.004(2)	0.003(3)	0	–0.002(2)	0
O(2)	4*c*	0.4447(7)	3/4	0.303(2)	0.005(3)	0.010(3)	0.005(3)	0	0.000(2)	0

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