Goethite, $\alpha$-FeO(OH), from single-crystal data

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Key indicators

Single-crystal X-ray study

\(T = 273\) K

Mean \(\sigma\)–O = \(0.001\) \(\text{\AA}\)

\(R\) factor = 0.019

\(wR\) factor = 0.052

Data-to-parameter ratio = 21.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

This is the first reported structure refinement of goethite, \(\alpha\)-FeO(OH), on the basis of a single-crystal X-ray diffraction study. The structure of goethite, isostructural with diaspore, AlO(OH), and groutite, MnO(OH), can be described in terms of a slightly distorted hexagonal close-packed O-atom arrangement with Fe atoms occupying one-half of the octahedral interstices, and with all atoms located on mirror planes. There are two distinct O sites, O1 and O2, each bonded to three Fe atoms, with O2 additionally bonded to an H atom. The O2–H...O1 donor–acceptor distance in goethite is significantly longer than that in diaspore or groutite, indicating that the hydrogen bonding in goethite is the weakest of the three minerals. Analysis of refinement data for the three isostructural compounds reveals rigid-body thermal motion behavior of the octahedral groups.

Comment

Goethite, \(\alpha\)-FeO(OH), is one of the most widespread forms of iron oxides in terrestrial soils, sediments and ore deposits (Cornell & Schwertmann, 2003; Strucki et al. 1988), as well as a common weathering product in rocks of all types (Ozdemir & Dunlop, 2000). It transforms to hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) between 453 and 543 K through dehydrogenation and has been used extensively in the preparation of maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)) in magnetic storage media. The crystal structure of goethite was first determined by Goldsztuaub (1935) and Hoppe (1940) using X-ray diffraction photographic techniques. Forsyth et al. (1968) and Szytula et al. (1968) examined the magnetic structure of goethite with neutron powder diffraction on both natural and synthetic samples and found that it is anti-ferromagnetic below about 373 K (the Néel point). The structural behavior of goethite as a function of temperature and pressure was investigated by Gualtieri & Venturelli (1999) and Nagai et al. (2003), respectively, by means of synchrotron X-ray powder diffraction. However, despite both its mineralogical and technological interest, no detailed structural information, such as anisotropic atomic displacement parameters, are available for goethite because of the lack of a single-crystal X-ray diffraction structure analysis.

Goethite is isostructural with diaspore, AlO(OH), and groutite, MnO(OH) (Forsyth et al., 1968; Szytula et al., 1968). Its structure can be described in terms of a slightly distorted hexagonal close-packed O-atom arrangement with Fe atoms occupying one-half of the octahedral interstices. The Fe\(^{3+}\)O\(_6\) octahedra share edges to form double chains running parallel to \(c\), which are further linked to form a three-dimensional structure by sharing vertices (Fig. 1). There are two distinct O sites, O1 and O2, both coordinated to three Fe atoms, with O2 additionally bonded to an H atom. In spite of the same ionic
radius of 0.645 Å for six-coordinated Fe$^{3+}$ and Mn$^{3+}$ ions (Shannon, 1976), the average M$^{2+}$—O bond length within the Fe$^{3+}$O$_6$ octahedron in goethite (2.026 Å) is slightly shorter than that within the Mn$^{2+}$O$_6$ octahedron in groutite (2.039 Å), due to the obvious Jahn–Teller effect of Mn$^{3+}$.

A translational– librational–screw (TLS) rigid-body analysis (Schomaker & Trueblood, 1968; Downs, 2000) was conducted on the FeO$_6$, AlO$_6$ and MnO$_6$ octahedral groups in goethite, diaspore (Hill, 1979) and groutite (Kohler et al., 1997), respectively. The atomic displacement parameters reveal rigid-body behavior with differences in the mean-square displacement amplitudes along the M—O bonds of less than 0.001 Å$^2$. The librational angles are small, at 1.7, 1.3 and 1.5° for goethite, diaspore and groutite, respectively. These magnitudes result in a very small thermal effect on the bond lengths. They are consistent with high-quality diffraction data, and with the edge-sharing topology of the double octahedral chains.

Hydrogen bonding is found between atom O2 of one FeO$_6$ octahedron and an O1 atom in an adjacent one, with an O2—H distance of 0.88 Å and an O2—H···O1' angle of 161 (3)$^\circ$. This value is comparable with that in diaspore [160.8 (1)°; Hill, 1979] but notably smaller than that in groutite [171 (4)°; Kohler et al., 1997]. The non-linear hydrogen bonding in goethite is known to be of moderate strength and represents the most common type of hydrogen bond (Jeffrey, 1997). Nevertheless, the donor–acceptor O2—H···O1' distance in goethite [2.747 (1) Å] is significantly longer than those in diaspore [2.649 (1) Å; Hill, 1979] or groutite [2.619 (1) Å; Kohler et al., 1997], indicating that the hydrogen bonding in goethite is the weakest of the three minerals. This observation is consistent with the IR spectroscopic measurements; the $\nu$OH stretching bands decrease from 3100 cm$^{-1}$ in goethite to 2950 cm$^{-1}$ in diaspore (Libowitzky & Rossman, 1997) and to 2685 cm$^{-1}$ in groutite (Kohler et al., 1997).

Experimental

The goethite crystal used in this study is a natural sample from Park County, Colorado, USA (RRUFF project collection, R050142; http://rruff.info). Within experimental uncertainty, the chemical composition determined with an electron microprobe is that of ideal FeO(OH).

Crystal data

\begin{align*}
\text{FeO(OH)} \\
M_r = 88.86 \\
\text{Orthorhombic, Pbnm} \\
\alpha = 4.5979 (2) \text{ Å} \\
b = 9.9510 (5) \text{ Å} \\
c = 3.0178 (1) \text{ Å} \\
V = 138.08 (1) \text{ Å}^3 \\
D_{\text{c}} = 4.275 \text{ Mg m}^{-3} \\
\mu = 10.30 \text{ mm}^{-1} \\
T = 273 (2) \text{ K} \\
\text{Crystal structure: SMART (Bruker, 2003); cell refinement: SHELXTL (Bruker, 1997).} \\
\text{Data collection: SMART (Bruker, 2003); cell refinement: SHELXTL (Bruker, 1997).} \\
\text{Selected bond lengths (Å).} \\
\text{Table 1}
\end{align*}

Table 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–O1i</td>
<td>1.9325 (9)</td>
<td>bond length</td>
</tr>
<tr>
<td>Fe–O2ii</td>
<td>1.9560 (6)</td>
<td>bond length</td>
</tr>
<tr>
<td>Fe–O2iii</td>
<td>2.0996 (9)</td>
<td>bond length</td>
</tr>
</tbody>
</table>

Consistent with previous studies, the non-standard setting Pbmn of space group Pbmn was used. The H atom was located in a difference Fourier map and its position was refined freely.

Data collection: SMART (Bruker, 2003); cell refinement: SHELXTL (Bruker, 2005); data reduction: SHELXTL; program(s) used to solve structure: SHELX97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XtalDraw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1997).

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References


