Hilgardite, Ca₂[B₅O₆]Cl·H₂O: a piezoelectric zeolite-type pentaborate

SUBRATA GHOSE AND CH'ENG WANG

Department of Geological Sciences, University of Washington
Seattle, Washington 98195

Abstract

Hilgardite, Ca₂B₅O₆Cl·H₂O, from Choctaw Salt Dome, Iberville Parish, Louisiana, is monoclinic, space group C2a, with unit-cell dimensions a = 11.438(2), b = 11.318(2), c = 6.318(1) Å, β = 90.06(1)º, and Z = 4. The crystal structure has been determined from three-dimensional Patterson and Fourier syntheses and refined by full-matrix least-square methods to an R-factor of 0.017 based on 1487 reflections, measured on an automatic single-crystal X-ray diffractometer. The absolute configuration and the hydrogen positions have been determined.

The structure of hilgardite is an open three-dimensional borate framework, whose building block is the anhydrous pentaborate polyanion [B₅O₆]³⁻, consisting of three (BO₄) tetrahedra and two (BO₃) triangles. The average tetrahedral and triangular B-O distances are 1.474 and 1.363 A respectively. The polyanions form three-tiered-repeating single chains (6.3 A c axis) by sharing tetrahedral corners with those belonging to adjacent polyanions. Within each chain, corners of two borate tetrahedra point along +a and +b directions, whereas corners of two borate triangles point along -a and -b directions; these corners are shared with four adjacent chains, such that tetrahedral corners of one chain are shared with triangular corners of the other. The resulting framework has ~6 and ~5 A diameter open channels parallel to the a and c axes respectively. The water molecules and the chlorine atoms within the channels form quasi-linear hydrogen-bonded chains parallel to the c axis. Hilgardite may be the precursor of a new family of borate zeolites.

The calcium atoms occur within channels parallel to the a and b axes. The [Ca(1)O₆Cl(H₂O)] and [Ca(2)O₆Cl₂] coordination polyhedra are slightly distorted pentagonal and hexagonal bipyramids, with average Ca-O distances 2.465 and 2.535 A, and average Ca-Cl distances 2.817 and 2.905 A respectively. By sharing opposite Cl corners the Ca(2) polyhedra form linear chains parallel to the a axis, crosslinked into a sheet by the Ca(1) polyhedra sharing polyhedral corners and edges. Hilgardite is mildly piezoelectric, the strongest electric axis being parallel to the a axis. The piezoelectricity along b is zero or nearly zero, because the borate triangles point alternately along +b and -b, whereas along the a axis, all borate triangles point along -a. All borate tetrahedra point along -c, the c axis presumably being the intermediate piezoelectric axis.

Introduction

The hydrated calcium chloroborate minerals hilgardite and parahilgardite were found in the insoluble residue from a brine well in the Choctaw Salt Dome, Iberville Parish, Louisiana, in association with anhydrite, danburite, boracite, dolomite, magnesite, caleite, quartz, sulphur, and other minerals (Hurlbut and Taylor, 1937, 1938; Hurlbut, 1938). Hilgardite occurs as colorless hemimorphic triangular plates. It is monoclinic, crystal class m. The lack of a center of symmetry is clearly indicated by the morphology, further confirmed by positive tests for piezoelectricity (Hurlbut, 1938). The unit-cell dimensions were determined by Hurlbut and Taylor (1937), who suggested the space group to be P2₁ or Pm, and the chemical composition as Ca₄(B₅O₁₁)₆Cl·4H₂O, which implies a close relationship to colemanite, Ca₅B₅O₁₅·5H₂O. Braitsch (1959) confirmed the unit-cell dimensions and found the correct space group to be Cc. In addition, he described a new triclinic strontiohilgardite phase, whose unit-cell volume is one-fourth that of hilgardite; on this basis, he suggested the chemical composition of hilgardite and
Hilgardite, $\text{Ca}_2[\text{B}_5\text{O}_9]\text{Cl}\cdot \text{H}_2\text{O}$.

A piezoelectric zeolite-type pentaborate

by

Subrsata Ghose and Che'ng Wan

Table 3. Hilgardite: observed and calculated structure factors
INDIVIDUAL ATOM PARAMETERS

*** THERMAL VALUES LISTED ARE MULTIPLIED BY ICO***

HILGAR

PAGE 3
<table>
<thead>
<tr>
<th>Scale Factors R-Values</th>
<th>New (Relative)</th>
<th>Old (Relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.072</td>
<td>0.178</td>
<td>0.178</td>
</tr>
<tr>
<td>1.077</td>
<td>0.178</td>
<td>0.178</td>
</tr>
</tbody>
</table>

**Reflection Statistics**

- Number of reflections: 0
- Number of reflections outside 0.1 to 1.0 range: 0
- Number of reflections less-than-2 sigma: 0
- Number of less-than-2 sigma reflections: 0
- Number of peaks in the asymmetric unit: 0

**Refl. Statistics**

- T: 1
- I: 1
- T: 1
- I: 1

**Predicted a Value of**

- 0.167 ± 0.015
| Angle | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z |
| 35°  | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 45°  | 15° | 25° | 35° | 45° | 55° | 65° | 75° | 85° | 95° | 105° | 115° | 125° | 135° | 145° | 155° | 165° | 175° | 185° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 60°  | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 90°  | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 120° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 150° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
| 180° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° |

Note: The table represents various angles and their corresponding values in different units.