Density functional theory (DFT) is used to determine positions of H atoms and to investigate hydrogen bonding in the crystal structures of two polymorphs of Cu₃(AsO₄)(OH)₃: clinoclase and gilmarite. Hydrogen bonds in clinoclase involve interactions between hydroxyl groups and O atoms of arsenate tetrahedra, whereas the crystal structure of gilmarite features OH…OH bonding, which is rather uncommon in copper hydroxy-oxysalts. Information-based parameters of structural complexity for clinoclase and gilmarite show that the former is more complex (IG,total = 213.212 bits/cell) than the latter (IG,total = 53.303 bits/cell), which indirectly points out that gilmarite is metastable. This suggestion is supported by the lower density of gilmarite (4.264 g/cm³) compared to that of clinoclase (4.397 g/cm³). The hypothesis of metastable character of gilmarite is in agreement with the Goldsmith’s simplicity principle and the Ostwald–Volmer rule.

Keywords: hydrogen bonding, clinoclase, gilmarite, density functional theory, structural complexity, metastability

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well. However, the role of structural complexity should not be neglected and one of the interesting problems that can be formulated is whether it is possible to use structural complexity measures to infer relative stability of different polymorphs?

Another interesting problem is whether structural complexity correlates with physical density of different polymorphs and how does it influence crystallization in natural systems. On the example of different copper oxy-salt systems, we have recently demonstrated that structural complexity as another expression of configurational entropy does correlate with the ease of crystallization. For instance, in the Ostwald cascade of the Cu₂(OH)₃Cl polymorphs (botallackite – atacamite – clinoatacamite), crystallization proceeds in the direction of increasing structural complexity, starting from simple (and less dense) botallackite and ending at most complex (and most dense) clinoatacamite (Krivovichev et al. 2017). In contrast, the Cu₃(PO₄)₂(OH)₃ polymorphs (pseudomalachite, ludjibaite and reichenbachite) do not differ essentially in their structural complexity, and this may explain their frequent simultaneous occurrence in nature and in synthesis experiments (Krivovichev et al. 2016b).

From this viewpoint, herein are considered two Cu₅(AsO₄)₃(OH)₃ polymorphs, clinoclase and gilmarite. In order to characterize fully their structural complexity, we report on the theoretical modeling of their hydrogen positions by means of the solid-state DFT method and use the obtained data to evaluate the hydrogen-bonding scheme and relative structural complexities of the two polymorphs.

2. Methods

2.1. Density functional theory (DFT) modeling

The CRYSTAL14 software package was employed for the solid-state DFT calculations (Dovesi et al. 2014). The Peintinger–Oliveira–Bredow split-valence triple-ζ (pob-TZVP) basis sets (Peintinger et al. 2013) were used for all atoms along with the hybrid Becke–3–Lee–Yang–Parr (B3LYP) functional, which provides excellent results for copper oxysalt crystals (Ruiz et al. 2006; Ruggiero et al. 2015; Krivovichev et al. 2016a, b). Geometry optimization was initiated with experimental determined crystal-structure models determined for clinoclase and gilmarite by Eby and Hawthorne (1990) and Sarp and Černý (1999), respectively (Tab. 1). The approximate positions of the H atoms have been proposed based on general crystal-chemical arguments. During the DFT optimization, all the non-H atom-positions and unit-cell parameters were kept constant, whereas the positions of the H atoms were allowed to relax. The unrestricted-spin calculation was used and the difference between α and β electrons was maintained for the first 10 cycles. The convergence criterion for the energy was set to 10⁻⁷ au. The optimized coordinates of the H atoms and the coordinates of the non-H atoms are given in Tabs 2 and 3 for clinoclase and gilmarite, respectively. Table 4 provides basic geometrical parameters of strong hydrogen bonds in both crystal structures.

2.2. Structural complexity calculations

In order to compare polymorphic variations in the system under study from the viewpoint of structural complexity, the latter was estimated as the Shannon information content per atom (Iₙ) and per unit cell (Iₙ(total)). According to this approach developed by Krivovichev (2012, 2013), the complexity of a crystal structure can be quantitatively characterized by the amount of Shannon information it contains measured in bits (binary digits) per atom (bits/atom) and
Hydrogen bonding in clinoclase and gilmarite

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per unit cell (bits/cell), respectively. The concept of Shannon information, also known as Shannon entropy, used here originates from information theory and its application to various problems in graph theory, chemistry, biology, etc. The amount of Shannon information reflects diversity and relative proportion of individual objects, e.g., the number and relative proportion of different sites in an elementary unit-cell of a crystal structure. The calculation involves the use of the following equations:

\[ I_G = - \sum_{i=1}^{k} p_i \log_2 p_i \text{ (bits/atom)} \quad (1), \]

\[ I_{G,\text{total}} = - v I_G = - v \sum_{i=1}^{k} p_i \log_2 p_i \text{ (bits/cell)} \quad (2), \]

where \( k \) is the number of different crystallographic orbits (independent crystallographic Wyckoff sites) in the structure and \( p_i \) is the random-choice probability for an atom from the \( i \)-th crystallographic orbit, that is:

\[ p_i = \frac{m_i}{v} \quad (3), \]

where \( m_i \) is a multiplicity of a crystallographic orbit (i.e. the number of atoms of a specific Wyckoff site in the reduced unit-cell), and \( v \) is the total number of atoms in the reduced unit cell.

The information-based structural-complexity parameters for the Cu4(AsO4)(OH)2 polymorphs were calculated using the TOPOS software package (Blatov et al. 2014) and are given in Tab. 1.

**Tab. 3 Atom coordinates for the crystal structure of gilmarite**

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.9987</td>
<td>0.0003</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cu1</td>
<td>0.0492</td>
<td>0.6036</td>
<td>0.3224</td>
</tr>
<tr>
<td>Cu2</td>
<td>0.5489</td>
<td>0.3631</td>
<td>0.3568</td>
</tr>
<tr>
<td>Cu3</td>
<td>0.5723</td>
<td>0.8811</td>
<td>0.3869</td>
</tr>
<tr>
<td>O1</td>
<td>0.1620</td>
<td>0.2710</td>
<td>0.0740</td>
</tr>
<tr>
<td>O2</td>
<td>0.1880</td>
<td>0.8050</td>
<td>0.0740</td>
</tr>
<tr>
<td>O3</td>
<td>0.7030</td>
<td>0.5420</td>
<td>0.1540</td>
</tr>
<tr>
<td>O4</td>
<td>0.7430</td>
<td>0.0600</td>
<td>0.1860</td>
</tr>
<tr>
<td>O5</td>
<td>0.3710</td>
<td>0.6730</td>
<td>0.3580</td>
</tr>
<tr>
<td>O6</td>
<td>0.4830</td>
<td>0.2230</td>
<td>0.6300</td>
</tr>
<tr>
<td>O7</td>
<td>0.9050</td>
<td>0.8680</td>
<td>0.6530</td>
</tr>
<tr>
<td>H1</td>
<td>0.6544</td>
<td>0.4384</td>
<td>0.9465</td>
</tr>
<tr>
<td>H2</td>
<td>0.3467</td>
<td>0.7231</td>
<td>0.7446</td>
</tr>
<tr>
<td>H3</td>
<td>0.3306</td>
<td>0.2383</td>
<td>0.7264</td>
</tr>
</tbody>
</table>

* coordinates of non-H atoms are from Sarp and Černý (1999); coordinates of H atoms are optimized using DFT method

**Fig. 1**

(a) The crystal structure of clinoclase projected along the \( b \) axis. (b) The sheet formed by \( \text{Cu}1\text{O}_4 \) and \( \text{Cu}2\text{O}_4 \) squares. (c) Two adjacent sheets that belong to the same layer. (d) Linkage of the two sheets by dimers of \( \text{Cu}3\text{O}_6 \) octahedra. (e) The whole layer with inserted \( \text{AsO}_4 \) tetrahedra.
In the crystal structure of clinoclase, the Cu1 and Cu3 sites are in distorted [4+2] octahedral coordination (four short and two long Cu2+–O bonds), whereas the Cu2 atom is coordinated by five O atoms to form a CuO5 square [4+1] pyramid (four short and one elongated Cu2+–O bonds; Ghose et al. 1965; Eby and Hawthorne 1990). The crystal structure is based upon two-dimensional layers parallel to (100) (Fig. 1a), which agrees well with the presence of perfect cleavage along this plane in clinoclase. The layers can be described as consisting of two sheets of the type shown in Fig. 1b. The Cu1O4 and Cu2O4 squares having short Cu2+–O bonds share the O3–O6 edge to form dimers that are linked via O5 atom to form chains parallel to the c axis. Two adjacent sheets (Fig. 1c) are linked by dimers of edge-sharing Cu3O6 octahedra (Fig. 1d). The (AsO4)3– tetrahedra are located within the layer (Fig. 1e). The layers are linked via long Cu2+–O bonds formed by the Cu1 and Cu2 atoms and via hydrogen bonds. The environments of the OH groups in clinoclase modeled by the DFT calculations are shown in Fig. 2a. There are three OH groups that form relatively strong two-center hydrogen bonds (see Tab. 4). The H–A bond lengths to the acceptor (A) O atoms are in the range of 1.846–1.919 Å, whereas the D–H–A angles (D = donor) vary from 148.87 to 165.11°. All acceptor O atoms belong to the arsenate groups. It is noteworthy that the OH5 and OH7 have additional close contacts (to O5 and O6 atoms, respectively), but it is unlikely that they correspond to meaningful hydrogen bonds. Both O6 and O5 atoms belong to hydroxyl groups, the H–O distances are longer than 2.45 Å, whereas the O–H–O angles are smaller than 98°.

The crystal structure of gilmarite is based on a three-dimensional framework consisting of layers of Cu polyhedra parallel to (001) and linked by (AsO4) tetrahedra.

**Tab. 4** Geometrical parameters of hydrogen bonding system in the crystal structures of clinoclase and gilmarite

<table>
<thead>
<tr>
<th></th>
<th>D–H</th>
<th>d(D–H) [Å]</th>
<th>d(H–A) [Å]</th>
<th>&lt;DHA [°]</th>
<th>d(D–A) [Å]</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoclase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O5–H1</td>
<td>0.965</td>
<td>1.912</td>
<td>148.87</td>
<td>2.783</td>
<td>O1</td>
<td></td>
</tr>
<tr>
<td>O6–H2</td>
<td>0.980</td>
<td>1.863</td>
<td>165.11</td>
<td>2.821</td>
<td>O3</td>
<td></td>
</tr>
<tr>
<td>O7–H3</td>
<td>0.979</td>
<td>1.846</td>
<td>164.17</td>
<td>2.801</td>
<td>O2</td>
<td></td>
</tr>
<tr>
<td>Gilmarite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3–H1</td>
<td>0.989</td>
<td>1.766</td>
<td>160.19</td>
<td>2.716</td>
<td>O6</td>
<td></td>
</tr>
<tr>
<td>O5–H2</td>
<td>0.986</td>
<td>1.818</td>
<td>159.39</td>
<td>2.762</td>
<td>O2</td>
<td></td>
</tr>
<tr>
<td>O6–H3</td>
<td>0.974</td>
<td>1.968</td>
<td>149.22</td>
<td>2.849</td>
<td>O1</td>
<td></td>
</tr>
</tbody>
</table>

*D = donor; A = acceptor

**Fig. 2a** – Coordination environments of hydroxyl groups in the crystal structure of clinoclase. **b** – Coordination environments of hydroxyl groups in the crystal structure of gilmarite.

### 3. Results

The crystal structure of gilmarite is based on a three-dimensional framework consisting of layers of Cu polyhedra parallel to (001) and linked by (AsO4) tetrahedra.
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viewpoint of the information amount per unit cell, the structural arrangement of gilmarite is much simpler than that of clinoclase. According to the Goldsmith’s simplicity principle (Goldsmith 1953) and its current interpretation (Krivovichev 2013, 2015), this may indicate that gilmarite is a metastable phase crystallized under some kinetically favored conditions. This suggestion is corroborated by the comparison of the values of physical density, which is equal to 4.264 g/cm³ for gilmarite and 4.397 g/cm³ for clinoclase. According to the Ostwald–Volmer rule (Holleman et al. 2001), for metastable crystallization, the less dense metastable phase forms first, due to the fact that, under supersaturation conditions, its nuclei reach their critical sizes faster than those of the stable phase (Fischer and Jansen 2002; Bach et al. 2013). The transformation from the metastable phase into a stable phase may occur along different routes that include: direct transformation (i.e. solid-state phase transition), solvent-mediated transformation (which includes dissolution of the metastable phase and precipitation of the stable one) and epitaxy-mediated transformation (when stable phase crystallizes on the surface of the metastable one) (Niekawa and Kitamura 2013). In the case under consideration, the direct gilmarite–clinoclase transformation must include phase transition of a reconstructive type, since the two structures are drastically different and may not be transformed one into another without breaking of the many chemical bonds. It is currently unclear which factors stabilize the formation of metastable gilmarite instead of stable clinoclase and understanding of these processes requires synthesis experiments.

4. Discussion

The structural complexity parameters for clinoclase and gilmarite given in Tab. 1 indicate that, from the viewpoint of the information amount per unit cell, the structural arrangement of gilmarite is much simpler than that of clinoclase. According to the Goldsmith’s simplicity principle (Goldsmith 1953) and its current interpretation (Krivovichev 2013, 2015), this may indicate that gilmarite is a metastable phase crystallized under some kinetically favored conditions. This suggestion is corroborated by the comparison of the values of physical density, which is equal to 4.264 g/cm³ for gilmarite and 4.397 g/cm³ for clinoclase. According to the Ostwald–Volmer rule (Holleman et al. 2001), for metastable crystallization, the less dense metastable phase forms first, due to the fact that, under supersaturation conditions, its nuclei reach their critical sizes faster than those of the stable phase (Fischer and Jansen 2002; Bach et al. 2013). The transformation from the metastable phase into a stable phase may occur along different routes that include: direct transformation (i.e. solid-state phase transition), solvent-mediated transformation (which includes dissolution of the metastable phase and precipitation of the stable one) and epitaxy-mediated transformation (when stable phase crystallizes on the surface of the metastable one) (Niekawa and Kitamura 2013). In the case under consideration, the direct gilmarite–clinoclase transformation must include phase transition of a reconstructive type, since the two structures are drastically different and may not be transformed one into another without breaking of the many chemical bonds. It is currently unclear which factors stabilize the formation of metastable gilmarite instead of stable clinoclase and understanding of these processes requires synthesis experiments.

Fig. 3a – The crystal structure of gilmarite projected along the b axis. b – The layer of Cu polyhedra (highlighted by grey color in Fig. 3a).
5. Conclusions

In conclusion, we have used density functional theory (DFT) methods to model hydrogen bonding schemes in clinoclase and gilmarite. Whereas hydrogen bonds in clinoclase involve interactions between hydroxyl groups and O atoms of arsenate tetrahedra, the crystal structure of gilmarite features the OH…OH bonding, which is rather uncommon for copper hydroxy-oxysalts. Information-theory considerations of structural complexity of clinoclase and gilmarite show that the former is more complex than the latter, which indirectly indicates that gilmarite is a metastable phase. This suggestion is supported by the lower density of gilmarite compared to that of clinoclase.

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