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Experimental and computational study of thaumasite structure

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ABSTRACT

The structure of thaumasite has been studied experimentally by means of a single crystal X-ray diffraction and FTIR methods, and theoretically using density functional theory (DFT) method. Very good agreement was achieved between calculated and experimental structural parameters. In addition, calculations offered the refinement of the positions of the hydrogen atoms. The detailed analysis of the hydrogen bonds existing in the thaumasite structure has been performed. Several types of hydrogen bonds have been classified. The water molecules coordinating Ca^{2+}cation act as proton donors in moderate O – H···O hydrogen bonds formed with CO$_3^{2-}$and SO$_4^{2-}$anions. The multiple O – H···O hydrogen bonds exist among water molecules themselves. Finally, relatively weak hydrogen bonds form water molecules with the OH groups from the coordination sphere of the Si(OH)$_6^{2-}$ anion. Further, calculated vibrational spectrum allowed complete assignment of all vibrational modes which are not available from the experimental spectrum that has a complex structure with overlapped bands, especially below 1500 cm^{-1}.

1. Introduction

Thaumasite is a relatively rare hydrated calcium silanol–carbonate–sulfate mineral with usual natural abundances in the wall rocks of sulfide mines, carbonate rocks, and more rarely in basaltic rocks. Its name is derived from the Greek word "*thaumasion*" meaning surprising.

The mineral samples can be collected i.e. in mid-European Alps, Sweden, Norway, Latin volcano, or Mururoa atoll. Thaumasite has also been detected in cement-based building materials as a negative technological consequence of thaumasite–sulfate attack [1]. The presence of thaumasite in concrete constructions represents a serious problem because thaumasite is a non-binder component and its increasing amount results in aging and degradation of the main cementitious binder phases in concrete(e.g. calcium silicate hydrates, C–S–H). Cement-based materials exposed to sulfate-bearing solutions such as some natural or polluted ground waters (external sulfate attack), or by the action of sulfates presented in the original cementitious mix (internal sulfate attack) have signs of deterioration. Sulfate ions react with ionic species of the pore solution to precipitate gypsum (CaSO$_4$·2H$_2$O), ettringite ([Ca$_3$Al(OH)$_6$·12H$_2$O]$_2$·(SO4)$_3$·2H$_2$O), thaumasite (Ca$_3$[Si(OH)$_6$·12H$_2$O]·(CO$_3$)·SO$_4$) or mixtures of these phases [2]. The precipitation of these solid phases can lead to a strain within the material inducing expansion, strength loss, and severe degradation [3]. In the thaumasite form of the sulfate attack (TSA), the C–S–H gel reacts with carbonate and sulfate ions forming thaumasite. Therefore, the C–S–H binding phase is consumed and, consequently, the strength of the concrete is significantly reduced.

The study of cement mineralogy is usually complicated due to fine-grained texture of cement matrix that, in general, precludes detailed structural investigation of cementitious compounds. Natural minerals – direct analogs of cement counterparts – give an excellent opportunity for in-depth understanding of crystal-chemical features of the latter, which, in turn, helps in predicting chemical behavior of corresponding artificial compounds. The structure of thaumasite is hexagonal (space group *P*6$_3$) and has some specific features that are typical for minerals from the ettringite family, to which thaumasite belongs too. The structure contains [Ca$_3$Si(OH)$_6$·12H$_2$O]$^{4+}$columns and sulfate and carbonate ions in an ordered arrangement in channels between the columns. It contains a lot of crystalline water (about 42 wt.%) that forms a rich network of hydrogen bonds with other structural components such as carbonate and sulfate ions. The water molecules also coordinate Ca^{2+}cations and are also involved in the hydrogen bonds with unusual structural unit — Si^{4+} cation coordinated by six hydroxyl groups. The first structure of thaumasite was published by Welin [4] without hydrogen positions and was followed by several crystallographic refinements including location of H positions (Edge and Taylor [5], Zemann and Zobetz [6], Effenberg et al. [7], and Jacobsen et al. [8]). The high quality X-ray powder diffraction (XRPD) data collected during the in situ time resolved heating process allowed a careful investigation of the structural changes occurring during decomposition and water removal in the thaumasite structure [9]. Recently, the single-crystal neutron diffraction study was combined with

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Raman spectroscopy [10] providing additional spectroscopic characterization of thaumasite to available experimental data from infrared (IR) studies. Varma and Bensted [11] and Hughes et al. [12] interpreted only a limited region in the IR spectrum. FTIR technique was used in the study of natural thaumasite samples from several localities revealing series of yet not described absorption bands in a region of 400–4000 cm^{-1} [13]. So far only one theoretical study of the structure of thaumasite exists [14]. In that study DFT method was used in a characterization of specific structural features including hydrogen bonding.

The presented work represents combined experimental and theoretical study of the thaumasite structure. Single crystal X-ray diffraction was performed in order to provide complete structural data of the natural thaumasite crystal sample. As standard X-ray method does not describe the position of light hydrogen atoms perfectly, DFT-based geometry relaxation of the atomic positions was performed to complete the structural information on the thaumasite structure. Based on the DFT relaxed structure the hydrogen bond analysis was performed. Further, a complete vibrational spectrum was calculated and used in the interpretation of the experimentally measured IR spectrum, which has a complex structure with overlapping bands and, consequently, its interpretation is problematic and not fully done yet.

2. Experimental details

A natural, transparent crystal sample of thaumasite (Fig. 1, ideal formula $Ca_3Si(OH)_6(CO_3)(SO_4)\cdot(H_2O)_{12}$) coming from the NCHwaning II mine in South Africa was received from Thames Valley Minerals company, which sells mineral specimens from the UK and around the world. The structural data were obtained by using single crystal X-ray diffraction method. Further, FTIR spectroscopy measurement was performed in a range of 400–4000 cm^{-1}.

2.1. Single crystal X-ray diffraction

The data were collected at 298.0 (1) K on an Oxford Diffraction Kappa geometry GEMINI R diffractometer equipped with Ruby CCD area detector using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 30 kV and 30 mA (Table 1). Distance from crystal to detector was 53 mm.

2.2. Infrared spectra

Infrared spectrum was collected by a Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer from Thermo Scientific. The KBr pressed disk technique (1 mg of sample and 200 mg KBr) was used to measure spectra in the middle infrared region (4000–400 cm^{-1}). Spectra were obtained by co-addition of 64 scans at a resolution of 4 cm^{-1}. Spectrum manipulations were performed using the Thermo Scientific OMNIC™ software package.

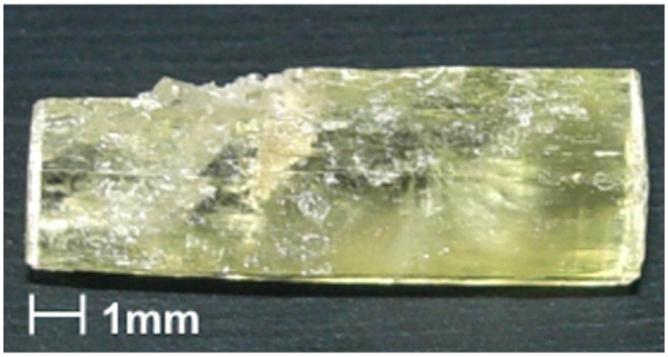

Fig. 1. Single crystal of thaumasite.

Table 1
Basic data and single crystal X-ray experimental details for thaumasite.

Chemical formula	$Ca_3Si(OH)_6(CO_3)(SO_4)\cdot 12H_2O$
Formula weight	622.65 g·mol^{-3}
Temperature, wavelength	293 (2) K, 0.71073 Å
Crystal system, space group	Hexagonal, $P\,6_3$
Unit cell dimensions	$a = 11.0460$ (2) Å $c = 10.4091$ (2) Å $\gamma = 120.0°$
Formula units per unit cell	2
Calculated density	1.880 g·cm^{-3}
Absorption coefficient	1.010 mm^{-1}
F (000)	652
Crystal size	1.070 × 0.601 × 0.536 mm
θ range for data collection	3.69° to 37.57°
Index ranges	$-18 \leq h \leq 16$ $-15 \leq k \leq 18$ $-17 \leq l \leq 17$
Max. and min. transmission	0.483 and 0.578
Reflections collected	31526
Independent reflections	3700 (R(int) = 0.0241)
Completeness to 2θ = 25.00	99.7%
Data/restraints/parameters	3700/11/124
Goodness-of-fit on F^2 1.041	1.116
Final R indices [I > σ(I)]	R1 = 0.0251, wR2 = 0.0716
R indices (all data)	R1 = 0.0257, wR2 = 0.0719
Largest diff. peak and hole	1.195 and −0.357 (eÅ^{-3})

3. Computational details

All calculations were performed using the Vienna Ab Initio Simulation Package, VASP [15,16], which is based on density functional theory (DFT). The exchange-correlation energy was described by the functional according Perdew, Burke, and Ernzerhof (PBE) [17], based on the generalized gradient approximation (GGA). The Kohn–Sham equations were solved variationally with a plane-wave (PW) basis set using an energy cut-off of 500 eV in the projector-augmented-wave (PAW) method [18,19]. Brillouin-zone sampling was restricted to the Γ-point only because of large computational cell. The initial structural model for calculations was taken from our single crystal X-ray data (collected in Table 2). The all atomic positions and lattice parameters were fully relaxed with no symmetry restriction ($P1$ symmetry). The relaxation criteria were 10^{-7} eV/atom for the total energy change, and 0.005 eV/Å for the maximal allowed forces acting on each atom. Normal modes of vibrations were calculated within the computational cells from the normal mode analysis accomplished in the frames of the harmonic approximation. The Hessian was constructed from the single point energy calculations on the $6n$ structures generated from the optimized structures by displacing each of the n atoms in the cell in positive and negative senses along the Cartesian directions x, y, z. Each pair of single point calculations was used to calculate the individual force constants [20].

4. Results and discussion

4.1. Structure of thaumasite

Conditions of the X-ray diffraction experiment together with the basic crystallographic data (space group and unit cell parameters) of thaumasite are given in Table 1. The structure was solved by direct methods [21] and refined by least-squares procedures on F^2. The drawing of the molecules was realized by means of the DIAMOND program [22]. Least-squares refinement was performed by minimizing the $\sum w(F_0^2 - F_c^2)^2$ function, where F_0 and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycle was $w = 1/[\sigma^2 F_0^2 + (0.0316P)^2 + 0.3316P]$, where $P = (F_0^2 + 2F_c^2)/3$. It is a well-known problem that conventional X-ray method does not provide an accurate localization of positions of hydrogen atoms in structure and for this purpose another approach (e.g. neutron diffraction) is needed. In our case, we decided to use computational DFT