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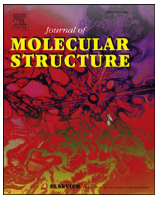

Structural and spectroscopic characterization of ettringite mineral –combined DFT and experimental study

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ABSTRACT

The structure of the ettringite mineral was studied by means of FTIR spectroscopy and single crystal X-ray diffraction method. The experimental study was combined with the first principle calculations based on density functional theory (DFT) method. Predicted structural parameters (unit cell vectors and positions of heavy atoms) are in a very good agreement with the experimental data. Moreover, calculations also enabled to refine the positions of the hydrogen atoms not determined precisely by the single crystal X-ray measurement. The detailed analysis of the hydrogen bonds in the ettringite structure was performed and several groups of the hydrogen bonds were classified. It was found that the water molecules from the coordination sphere of Ca^{2+} cations act as proton donors in moderate O–H···O hydrogen bonds with SO_3^{2-} anions. Further, multiple O–H···O hydrogen bonds were identified among water molecules themselves. In addition, also hydroxyl groups from the $[Al(OH)_6]^{3-}$ octahedral units are involved in the weak O–H···O hydrogen bonding with the water molecules. The calculated vibrational spectrum showed all typical features observed in the experimental FTIR spectrum. Moreover, performing the analysis of the calculated spectrum, all vibrational modes were distinguished and assigned. Such a complete analysis of the measured IR and/or Raman spectra is not fully possible, specifically for the region below 1500 cm^{-1}, which is characterized by a complex curve with many overlapped bands. A comparison of the vibrational spectra of ettringite and thaumasite (mineral structurally similar to ettringite) revealed the origin of the most important differences between them.

1. Introduction

Portland cement is one of the most frequently used building materials around the world. In reaction with water, hydration phases are formed representing main binders in concrete material. Detailed study of the hydration mechanisms and also of the structure of the hydration products is important for the use of cementitious pastes and concrete in the building industry. Several natural calcium-alumino-silicate (CAS) minerals, direct analogs of cement counterparts, offer good opportunity for in-depth understanding of the structural and chemical features of cement and concrete. Ettringite, boro-ettringite and thaumasite are typical CAS compounds constituting an ettringite group of minerals. Ettringite is a hexacalcium aluminate trisulfate hydrate mineral (ideal formula $Ca_6[Al(OH)_6]_2(SO_4)_3.{\sim}26H_2O$) formed during Portland cement hydration. Its formation in the early cement hydration stage plays an important role in controlling the setting rate of the highly reactive aluminate phases and its formation results in a volume increase in the fresh, plastic concrete, which has also been associated spatially with severe cracking in cured hardened concrete during what is referred to as delayed ettringite formation (DEF) and during cement degradation via sulfate attacks [1]. The sulfate ions react with ionic species of the pore solution to precipitate gypsum, ettringite, thaumasite or mixtures of these phases [2]. Sulfate attack from external sources is described, including processes resulting in the formation of ettringite and thaumasite, in the work by Glasser et al. [3].

Although thaumasite and ettringite are from the same family of minerals, several differences exist between their structures. Apart from the hexagonal structure of thaumasite (space group $P6_3$), the

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ettringite structure is trigonal (space group $P31c$). Further, ettringite contains Al atoms instead of Si, and three SO_4^{2-} anions and two H_2O molecules replace two SO_4^{2-} and two CO_3^{2-} ions. The structural columns, a typical feature for both minerals, are essentially similar and a difference in the *c* parameter and symmetry arises from the ordering of the sulfate anions in ettringite [4]. The ordered arrangement of the intercolumn material leads to the halving of the *c*-dimension of the unit cell in thaumasite [5]. The structures of thaumasite and ettringite were reported first time by Edge and Taylor [6], followed by the work of Moore and Taylor [7]. Both structures have been refined later [8–11], with the reported structures agreeing with the earlier works except fine structural details.

Selected area electron diffraction (SAED) patterns were obtained in the study of the structure of ettringite, carbonate ettringite, and thaumasite [4] and it was revealed that the presence of carbonate in ettringite hinders water loss preventing the movement of the columns along the *a* axis and also reducing the shrinkage along the *c* direction. Vibrational spectroscopy, specifically the Fourier Transform infrared spectroscopy (FTIR), was used to obtain a local symmetry and structural information of reactive groups such as OH and H_2O presented in the ettringite structure [12]. FTIR analysis together with the XRD and EDX (Energy Dispersive X-ray) methods was used in the analysis of the structure of ettringite [13], synthetized ettringite [14], solid solutions of thaumasite and ettringite [5], and hydrated Portland cement [15]. These studies reported an assignment of several well-distinguished bands to vibrational modes of the basic functional groups (e.g. stretching and bending of $-OH$, CO_3^{2-}, SO_4^{2-}, $[Si(OH)_6]^{2-}$, and $[Al(OH)_6]^{3-}$ groups) later complemented by the interpretation of Raman spectra [12,16]. However, a complete analysis of both IR and Raman spectra is not possible because both spectra are complicated with many overlapping unresolved bands; thus, their identification can be problematic.

Computational chemistry represents very useful tool for description and analyzing the structure and properties of compounds. For example, calculated frequencies can be unambiguously assigned to particular vibrational modes and types of vibrations can be determined from the corresponding eigenvectors. In our recent paper this type of analysis was performed on the measured IR spectrum of thaumasite by means of the DFT-calculated vibrational modes [17]. The DFT method was also used in earlier study by Drábik et al. [18] for a characterization of specific structural features of thaumasite including hydrogen bonding.

The present work reports combined experimental (single crystal X-ray and FTIR) and theoretical studies of the ettringite structure with the aim to provide complete structural and spectroscopic data of the natural ettringite crystal sample. DFT-based geometry relaxation of the all atomic positions is performed to complete the structural information on the position of hydrogen atoms followed by the hydrogen bond analysis. Further, vibrational spectrum, first time calculated at *ab initio* level, is used in a complete assignment of frequencies helping to understand all features of experimental IR and Raman spectra. Finally, the main differences between the IR spectra of thaumasite and ettringite are explained with respect to structural and compositional differences of both minerals.

2. Experimental details

A natural, yellow crystal sample of the ettringite mineral (Fig. 1) was obtained from Wessels Mine, Nothern Cape Province, South Africa. The structural data were derived by single crystal X-ray diffraction and FTIR spectrum was measured in a range of 400–4000 cm^{-1}.

Fig. 1. Ettringite sample.

The single crystal X-ray 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. Distance from crystal to detector was 53 mm. The crystallographic data of ettringite together with the conditions of the X-ray diffraction measurement are given in Table 1.

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

3. Computational details

All calculations were performed using the Vienna Ab Initio Simulation Package, VASP [19,20], built on DFT method. In the used PBE functional, the exchange-correlation energy is described according Perdew, Burke, and Ernzerhof [21] approach, based on the generalized gradient approximation (GGA). The Kohn–Sham equations are solved variationally using plane-wave (PW) basis set and projector-augmented-wave (PAW) method [22,23]. All calculations were performed by applying an energy cut-off of 500 eV. The Brillouin-zone sampling was restricted to the *gamma*-point only because of a large computational cell. The initial structural model for calculations was taken from our single crystal X-ray data collected in Tables 1–3. 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 frame of harmonic approximation using a finite difference method and fixed parameters of the computational cell. The Hessian was constructed from the single point energy calculations on the $6n$ structures generated from the completely optimized structure by displacing each of the n atoms in the cell in positive and negative senses along the Cartesian directions *x*, *y*, and *z*. Each pair of single point calculations was used to calculate the individual force constants [24]. No scaling factor was used in the comparison with experimental data.