**Investigation on the stability, electronic, optical and mechanical properties of novel calcium carbonate hydrates via first-principles calculations**

Yunxuan Zhoua, Mingyu Hua,c, Gengsen Xua, Ruiju Xua, Xiaoyu Chonga,b\*, Jing Fenga

a*Faculty of Materials Science and Engineering,* *Kunming University of Science and Technology,*

*Kunming, 650093, P, R, China*

b *Department of Materials Science and Engineering, Pennsylvania State University,*

*University Park, PA 16802, USA*

c *School of Engineering, Brown University, Providence, RI 02912, USA*

*Corresponding author：**xuc83@psu.edu (X.Y. Chong)*

**Abstract**:Calcium carbonate (CaCO3) is an inorganic compound which is widely used in industry, chemistry, construction, ocean acidification and biomineralization due to its rich constituent on earth and excellent performance, in which calcium carbonate hydrates are important systems. In Z.Y. Zou et al’s work *(Science*, 2019, 363, 396–400), they found a novel calcium carbonate hemihydrate phase, but the structure stability, optical and mechanical properties has not been studied. In this work, the stability, electronic, optical, and mechanical properties of novel calcium carbonate hydrates were investigated by using the first-principles calculations within density functional theory (DFT). CaCO3·*x*H2O (*x=*1/2, 1 and 6) are determined dynamically stable phases by phonon spectrum, but the Gibbs energy of reaction of CaCO3·1/2H2O is higher than other calcium carbonate hydrates. That’s why the CaCO3·1/2H2O is hard to synthesize in the experiments. In addition, the optical and mechanical properties of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are expounded in detail. It shows that the CaCO3·1/2H2O has the largest bulk modulus, shear modulus, Young’s modulus with the values 60.51, 36.56 and 91.28 GPa with respect to other two calcium carbonate hydrates investigated in this paper. This work will provide guidance for experiments and its applications, such as biomineralization, geology, and industrial processes.

**Keywords:** First-principles calculations; Calcium carbonate hydrates; Phonon; Optical properties; Mechanical properties

**1. Introduction**

Calcium carbonate (CaCO3) is inorganic compounds which can be commonly found on earth and is widely used in geological, biological, technological concerns, industry, chemistry, construction, ocean acidification and biomineralization, etc.[[1](#_ENREF_1), [2](#_ENREF_2)] CaCO3 is an important part of the global carbon cycle. It releases CO2 solidified in rocks into the atmosphere through weathering, on the other hand, calcium carbonate can re-fix CO2 in the atmosphere under the process of sedimentation.[[3](#_ENREF_3)] Over the past few decades, a lot of researches have been done on three anhydrous crystalline polymorphs of CaCO3, including calcite, aragonite, and vaterite, while two of them were hydrated crystalline phases—monohydrocalcite[[4](#_ENREF_4), [5](#_ENREF_5)] (CaCO3·1H2O) and ikaite [[6](#_ENREF_6), [7](#_ENREF_7)] (CaCO3·6H2O). What’s more, in the recent research, an interesting calcium carbonate hemihydrate with monoclinic structure has been unexpectedly discovered for the first time by Z.Y. Zou. et al[[8](#_ENREF_8)]. Whose discovery expanded our knowledge of the CaCO3 family and implicated in biomineralization, geology, and industrial processes.

With the development of computing, materials computational science is an effective means of simulation in both computational accuracy and computational efficiency. While the first-principles calculations is one of excellent effective tools to calculate the properties of materials including metal material, inorganic non-metal material, biological materials, functional materials, semiconductor materials and composite materials, etc. The vibrational spectrum of calcite had been researched through an ab initio quantum-mechanical calculation by M. Prencipe. et al[[9](#_ENREF_9)] who found this method was in agreement with experimental values. Moreover, a large number of articles about the experimental and theoretical researches of calcium carbonate hydrates were appeared. Monohydrocalcite and ikaite were research by many scholars have studied over the last few decades. Monohydrocalcite was a rare mineral in geological settings, which can be found in seawater environment and played a role inremediation material for hazardous oxyanions.[[5](#_ENREF_5), [10](#_ENREF_10)]. It was also regarded as an adsorbent to remove phosphate from solution and the mechanism of phosphate on monohydrocalcite including ionic strengths, reaction times, and temperatures, etc., which were discussed elaborately by S Yagi et al[[11](#_ENREF_11)]. In addition, the structures of both CaCO3·6H2O and CaCO3·1H2O had been studied by R Demichelis et al through the PBE0 level of theory[[12](#_ENREF_12)]. A.M Chaka [[13](#_ENREF_13)] had researched the thermodynamics of hydrated calcium carbonates and calcium analogues of magnesium carbonates by ab initio. In order to determine the stability of calcium carbonate polymorphs, the incorporation ab initio thermodynamics based on density-functional theory and experimental chemical potentials for H2O-rich and CO2-rich systems were used. Furthermore, she also discussed carbonate crystallization pathways in detail. The hydrogen bonding in ikaite was investigated by I. P Swainson et al[[14](#_ENREF_14)]. They found the linear thermal expansion coefficients were quite anisotropic due to being smaller in the direction of the C-O bond. In addition, S.N Costa et al[[15](#_ENREF_15)] hadbeen researched the structure, electronic, optical and vibrational properties of hydrated calcium carbonate crystals CaCO3·(1H2O,6H2O).

To our best knowledge, there are no articles to investigate the electronic, optical and mechanical properties of calcium carbonate hydrates for the novel CaCO3·1/2H2O, which limits their applications for the controlling the formation of crystalline calcium

carbonates, biominerals and global carbon cycle, etc. Therefore, in this work, the structural stability, electronic, optical and mechanical properties of calcium carbonate hydrates (CaCO3·*x*H2O; *x=*1/2, 1 and 6) are investigated by the first-principles calculation, which provide guidance for experiment and its application, such as biomineralization, geology, and industrial processes.

**2. Computational method and details**

Calcium carbonate hemihydrate (CaCO3·1/2H2O)[[8](#_ENREF_8)] has a monoclinic structure, belonging to the P121/c1(14) space with lattice parameters *a*=9.64 Å, *b*=10.47 Å and *c*=6.42 Å. The structure of monohydrocalcite (CaCO3·1H2O)[[4](#_ENREF_4), [5](#_ENREF_5)] is selected as space group: P31(144) with lattice parameters *a*=10.65 Å, *b*=10.65 Å and *c*=7.64 Å. While ikaite (CaCO3·6H2O)[[7](#_ENREF_7)] belongs to C12/c1 space group (No.15) with lattice parameters *a*=8.78 Å, *b*=8.28 Å and *c*=10.88 Å.

In this work, all calculations were conducted using the Cambridge Serial Total Energy Package (CASTEP) codes based on the density functional theory (DFT) [[16](#_ENREF_16)], which was the first-principles plane wave pseudopotential method. Ultra-soft pseudopotentials (USPPs)[[17](#_ENREF_17)] were used for describing the interaction between atomic core and valence electrons in reciprocal space were used, and the valence electron configurations for C, H, Ca and O atoms were 2*s*22*p*2, 1*s*1, 3*s*23*p*64*s*2 and 2*s*22*p*4, respectively. After careful test, 4×4×6, 5×5×8 and 6×8×4 grid of Monkhorst-Pack special *k*-points in the Brillouin zone (BZ) were used for bulk models CaCO3·1/2H2O, CaCO3·1H2O and CaCO3·6H2O, respectively. In order to ensure the calculations converged for calculation accuracy, the maximum plane-wave basis cutoff energy was 450 eV. The exchange correlation potential within generalized gradient approximation (GGA) was described the Perdew-Burke-Ernzerhof (PBE)[[18](#_ENREF_18)] and a DFT-D dispersion correction with grimme method was adopted in all calculations to improve the calculation accuracy for weak interaction. During the structural optimization process, Broyden-Fletcher-Goldfarb-Shanno (BFGS)[[19](#_ENREF_19)] method was used until the total energy changes were converged to 1×10-9 eV/atom, self-consistent field convergence to 2×10-6 eV/atom, maximum force 0.03 eV/Å, respectively. Elastic constants of a solid were calculated by an efficient strain-stress method through a linear least-square fit of the first-principle calculating stress versus strain. The phonon dispersion curves of CaCO3·1/2H2O, CaCO3·1H2O and CaCO3·6H2O were calculated according to the finite displace method.

**3. Result and discussion**

*3.1 Crystal structure and phonon dispersion*

The calculated crystal structures of calcium carbonate hemihydrates (CaCO3·1/2H2O), monohydrocalcite (CaCO3·1H2O) and ikaite (CaCO3·6H2O) are shown in Fig. 1(a)-(c). CaCO3·1H2O, CaCO3·6H2O and CaCO3·1/2H2O have a hexagonal unit cell containing 9 formula units, 4 formula units and 8 formula units, respectively. From the basic chemical knowledge, it is well known that one C atom and three O atoms constitute. Due to the different crystal structure, these forms show great differences in physical properties, which are mainly reflected onstructural stability. And the specific chemical reaction equation of calcium carbonate hydrates during formation can be expressed as:

 (1)

 (2)

 (3)

Obviously, the equation from (1) to (3) are different value of H2O, which cause various calcium carbonate hydrates with different crystal structure, indicating difference physical properties and mechanical properties. What’s more, the calculated X-ray diffraction of CaCO3·*x*H2O (*x=*1/2, 1 and 6) isshow in Fig. 1(d). The main peak are appearedat 16 to 21 degree But there are two nearly same intensity peaksat 2 theta as 17 and 34 degree for CaCO3·6H2O. The peaks of CaCO3·*x*H2O (*x=*1/2, 1 and 6) increases significantly with the increase of water content at 55 to 70 degree. In Fig. 1(e), the calculated XRD values of CaCO3·1/2H2O are good agreement with the experimental ones by Z.Y Zou et al in the reference [8].

The Gibbs energy of reaction (ΔGr) at 0 K for CaCO3+H2O is very important to judge the stability and formation possibility of CaCO3·*x*H2O (*x=*1/2, 1 and 6), which can be expressed by the following formula,

** (4)

where  is the total energy of CaCO3·*x*H2O (*x=*1/2, 1 and 6),  is the energy of CaCO3, and  represents the energy of water molecule, m and n represent the number of CaCO3 and H2O, respectively. N is the total number of atoms in CaCO3·*x*H2O (*x=*1/2, 1 and 6). The calculated ΔGr, total energy, the energy of water molecule and CaCO3 are shown in table 1. Generally speaking, the smaller the ΔGr is, the more possible the compounds to form. From table 1, the ΔGr decreases with H2O increases, indicating the CaCO3·6H2O is the most stable calcium carbonate hydrates. The stability of these calcium carbonate hydrates form the following sequence: CaCO3·6H2O > CaCO3·H2O > CaCO3·1/2H2O.

Furthermore, we can obtain the lattice parameters, density, volume and density of calcium carbonate hydrates after optimizing these crystal structure, which are listed in table 2. Obviously, the calculated values are slightly larger than the results from the theoretical and experimental values [[7](#_ENREF_7), [14](#_ENREF_14), [15](#_ENREF_15), [20](#_ENREF_20), [21](#_ENREF_21)]. What’s more, in this work, the calculated lattice parameters by using PBE+TS functional are slightly different from those obtained by other methods, such as B3LYP-D2 and PBE-D2. The discrepancy between the calculated value and the experimental value probably comes from lattice defects, the effect of temperature on crystal structure, experimental environment and different approximation functions. However, the calculation method is reasonable because these differences are very small. On the other hand, CaCO3·1/2H2O has the maximum density with the value of 2.23 g.cm-3, while the CaCO3·6H2O has the minimum values of 1.86 g.cm-3, which is in agreement with the experimental values as 2.38 g.cm-3 for CaCO3·1H2O and 1.8 g.cm-3 for CaCO3·6H2O.[[22](#_ENREF_22), [23](#_ENREF_23)]

The calculated phonon dispersion curves of the calcium carbonate hydrates along the high symmetry direction in the Brillouin zone are shown in Fig. 2. The calculated phonon spectra of CaCO3·*x*H2O (*x=*1/2, 1 and 6) show no soft modes at any high-symmetry dispersion, suggesting that these calcium carbonate hydrates are dynamic stable[[24-28](#_ENREF_24)], which proves the experimental point that calcium carbonate contains water is dynamic stable. These stable calcium carbonate hydrates contain 1/2, 1 and 6 H2O. Especially for the CaCO3·1/2H2O, the calculated phonon dispersions are remarkable consistent with the experimental values, which represent with the red hollow circle in Fig. 2(a), and the experimental data were obtained from the ref. [8]. Calcium carbonate and water react to stable hydrates with high energy barrier, which is harder to transform or decompose. Moreover, the phonon density of states for calcium carbonate hydrates is shown in Fig. 2, which corresponds to the phonon dispersion curves, and the higher-frequency vibrations are mainly contributed by the dynamics of the H2O molecule.

*3.2 Electronic structure and chemical bonding characteristic*

As we all know that band structure helps us to distinguish the electrical behavior of the compound: whether the compound is the conductor, semiconductor or insulator. The band structure and total density of states (TDOS) and partial density of states (PDOS) of hydrated crystalline calcium carbonate are shown in Fig. 3. We focus on the band shape near the Fermi level, therefore, we don't draw the energy band away from it. From Fig. 3, most obviously, they exhibit indirect insulating properties. At the G point, the valence bands of the CaCO3·*x*H2O (*x=*1/2, 1 and 6) are very flat, while the conduction band has some curvatures, indicating that the effective masses of holes are much larger than the electron masses. In order to grasp and describe the structural stability, the TDOS and PDOS are discussed here and shown in Fig. 3(b), (d) and (f). The calculated values of TDOS for all calcium carbonate hydrates are nearly zero at Fermi energy (EF), indicating that they have covalent-ionic feature. What’s more, it is clearly observable that the TDOS of calcium carbonate hydrates are primarily contributed by the H-1*s*, C-2*p* and O-2*p* state near the EF. From the 5 to 8 eV, H-1*s* and C-2*p* states are the main effects to TDOS. Furthermore, the charge interaction near EF forms the C-O ionic bond, reflecting hybridization between C and O orbital. Furthermore, we can see that the valence band maximum (VBM) is mainly contributed by the O-2*p* orbital, while the conduction band minimum (CBM) is mainly contributed by the C-2*p* orbital. The energy gaps of the calcium carbonate hydrates around the Fermi level are 4.571 eV (B→G transition from valence band to conduction band), 5.069 eV (A→G transition from valence band to conduction band) and 5.336 eV (Z→G transition from valence band to conduction band) for CaCO3·1/2H2O, CaCO3·6H2O and CaCO3·H2O, respectively, which are in agreement with the calculated values (monohydrated: 5.53-5.60 eV; hexahydrated: 5.14eV) by Costa S.N. et al.[[15](#_ENREF_15)]. The error range is 0.071eV to 0.264eV between them due to different calculated parameters, indicating the calculation method is accurate.

The calculated charge densities of calcium carbonate hydrates are presented in (100) planes and shown in Fig 4. The blue region and red region represent the accumulation of electronic charge and the depletion of electronic charge, respectively. It further indicates that C-O ionic bonds are observed in calcium carbonate hydrates, which conforms to analysis on the TDOS and PDOS in Fig. 3. What’s more, we can clearly see that calcium carbonate hydrates hascomplex bonding. CO32+ has the covalent-ionic bonds for all calcium carbonate hydrates, which can find in Fig. 4. What’s more, in order to describe the bond strength quantitatively, the Mulliken’s overlap bond population is employed in this work, and the detail discussion can be found in the supplementary materials in Fig. S1, Fig.S2 and Table S1.

*3.3 Optical properties*

As we all know that the macroscopic optical response function of solids can be described by the complex dielectric function, which can be used following equation:  (5)

where ; . The reflectivity, conductivity, absorption and others properties of calcium carbonate hydrates can be derived with the definition of direct transition probability and the Krames-Kroning dispersion relation[[29](#_ENREF_29), [30](#_ENREF_30)]:

 (6)

 (7)

 (8)

 (9)

Where *C, V* represent conduction band and valence band, respectively. BZ, *K* and  are the first Brillouin zone, reciprocal vector, angular frequency, respectively.  the eigenvalue of conduction band and valence band, respectively. *n* and *k* are the reflection coefficient and extinction coefficient. The optical properties including dielectric function, reflectivity, conductivity, absorption, refractive index and loss function of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are shown in Fig. 5 (a)-(f). Imaginary part of dielectric function is shown in Fig. 5(a), we can clearly see a peak appear in 7.5 eV. This results can be proved from the density of state in Fig. 3. Furthermore, from Fig. 5 (b), we can know that the reflectivity of CaCO3·*x*H2O (*x=*1/2, 1 and 6) decreases with the increase of water, which conforms to the band gap in the Fig. 3. CaCO3·1/2H2O has the largest reflectivity, while CaCO3·6H2O has the smallest reflectivity when the frequency value is about 8.0 eV. It's obvious that the transmittance of light is positively correlated with the refraction of light. It is beneficial to the lens because of its high refractive index. Therefore, the CaCO3·1/2H2O has the potential as luminescent material. The optical properties of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are huge difference due to the different structures and different position of water. What’s more, the conductivities of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are shown in Fig. 5 (c). The peak of photoconductivity mainly occurs in 7 eV for the CaCO3·1/2H2O and CaCO3·H2O, while the CaCO3·6H2O has other peak with 26 eV, indicating the H2O is the main factor affecting conductivity. The absorption of CaCO3·*x*H2O (*x=*1/2, 1 and 6) decreases with the increase of water, and the Loss function has a similar regularity. The dielectric loss can be expressed as follows:

 (10) which is the imaginary part of dielectric constant. Both the imaginary part and the real part of the refractive index decrease with the increase of the water content. Therefore, the dielectric function, reflectivity, conductivity, absorption, refractive index and loss function of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are decrease with the H2O increases.

*3.4 Anisotropic elastic properties*

The elastic stiffness tensor elements *Cij* of the calcium carbonate hydrates are calculated via first-principles calculations with the stress-strain method based on the general Hooke’s law.[[31](#_ENREF_31)] These elastic constants and modulus results are listed in Table 3. *Cij* is the vital mechanical property, which is very beneficial to understanding the mechanical properties of calcium carbonate hydrates. In this work, we also calculate all elastic constants of the calcium carbonate hydrates which are mechanically stable on the basis of the Born-Huang’s criterions [[32](#_ENREF_32), [33](#_ENREF_33)]and the specific criteria can be found in reference [26]. CaCO3·1/2H2O with monoclinic structure is not easy to be compressed under the external uniaxial stress along the [001] and [010] directions because it has the largest *C*11 and *C*22 with 109.28 GPa and129.65 GPa, respectively. While CaCO3·6H2O is easy to be compressed along a-axis and b-axis compared with other calcium carbonate hydrates. The deformation resistance of these calcium carbonate hydrates is determined by many factors such different crystal structures and orientation of bonds. *C*12 characterizes resist shear deformation at (100) crystal plane along the  direction. In Table 3, the *C*12 value of CaCO3·1/2H2O is 36.33 GPa which is larger than other calcium carbonate hydrates, indicating that it is hard to be shear deformation along  direction.

When elastic constants (*Cij*) if calcium carbonate hydrates are obtained, the polycrystalline modulus including bulk and shear modulus iscalculated according to the elastic constants matrix[[33](#_ENREF_33)], which can be see the attachment for details. In order to further apprehend the mechanical anisotropy of CaCO3·*x*H2O (*x=*1/2, 1 and 6), the three-dimensional (3D) surface of Young’s modulus for them are plotted in Fig. 6. The 3D representation of Young’s modulus is given by the following equations:

For the hexagonal structure (CaCO3·1H2O) [[34](#_ENREF_34)]

 (11)

For the monoclinic structure (CaCO3·1/2H2Oand CaCO3·6H2O)

 (12)

Where  represents the elastic compliance constants,,  and  are the directional cosines in spherical coordinates with respect to *θ* and *φ* (). As shown in Fig. 6, CaCO3·6H2O displays strong anisotropy because the shapes are deviated from the perfect sphere. CaCO3·1/2H2O also represents strong anisotropy, while CaCO3·H2O shows weak anisotropy because the graph is close to a sphere. These results are in agreement with the universal anisotropic index (*A*U) and the specific formula for*A*U and percent anisotropic index(*AB* and *AG*) as following [[35](#_ENREF_35)].

 (13)

 (14)

 (15)

where *BV, BR, GV* and *GR* represent the bulk modulus and share modulus estimation within Voigt and Reuss approximations, respectively. The anisotropy index of CaCO3·*x*H2O (*x=*1/2, 1 and 6) can be determined by the value zero, if the value is very close to zero, it indicates the less anisotropy, vice versa. The results are listed in Table 3. CaCO3·6H2O has the highest values of the *AU*, indicating that the elastic properties of CaCO3·6H2O havethe strongest anisotropy. Similarly, the value of *AG*, *AB* also confirmed this results. From Table 3, the universal anisotropic index of CaCO3·*x*H2O (*x=*1/2, 1 and 6) formedthe following sequence: CaCO3·6H2O (0.742) > CaCO3·1/2H2O (0.454) > CaCO3·H2O (0.155). We can clearly see that the Young’s modulus of these three calcium carbonate hydrates hasdifferent surface constructions due to the different crystal structures. Furthermore, planar projections of the Young’s modulus of the calcium carbonate hydrates on the (001) and (110) crystallographic planes are shown in Fig. 6. The anisotropy of Young’s modulus for all the calcium carbonate hydrates on the (110) plane is stronger than (001) plane. What’s more, CaCO3·6H2O has the strongest anisotropy of Young’s modulus among them due to the most remarkable anisotropic geometry of the surface contour.

Intrinsic hardness (*HV*) is also an important index for the calcium carbonate hydrates because their application is not indirectly related to the hardness. In our work, we choose Chen's model[[36](#_ENREF_36)] and Tian's model[[37](#_ENREF_37)] to calculate the hardness of the calcium carbonate hydrates, which can be expressed as follows:

 (16)

 (17)

where *k* is the Pugh ratio as *B/G.* It is clearly seen that the values of hardness are excellent close through Chen's model and Tian's model. CaCO3·6H2O has the largest hardness with 6.386 GPa, while CaCO3·H2O has the smallest with 4.274 GPa due to different atomic constitute and disparate hydrates. In Tian's model, the hardness of calcium carbonate hydrates comply with following sequence: CaCO3·1/2H2O > CaCO3·6H2O > CaCO3·H2O.

**4. Conclusions**

In summary, the structural stability, electronic, optical and mechanical properties of calcium carbonate hydrates are investigated in detail by first-principles calculations based on density functional theory in the present work. Firstly, the calculated phonon distribution curves of calcium carbonate hydrates are analyzed and find they are dynamic stability without no soft mode. Then, based on the analysis of the electronic structure and Mulliken’s overlap bond population of calcium carbonate hydrates, they have strong covalent-ionic character. What’s more, the optical properties of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are expounded in detail. It shows that dielectric function, reflectivity, conductivity, absorption, refractive index and loss function of CaCO3·*x*H2O (*x=*1/2, 1 and 6) are decrease with the H2O increases. Finally, the elastic stiffness tensors of calcium carbonate hydrates are calculated. CaCO3·1/2H2O has the largest bulk modulus, shear modulus, Young’s modulus as 60.51 GPa, 36.56 GPa and 91.28 GPa, respectively. But CaCO3·1/2H2O has the highest Gibbs energy of reaction. Therefore, this work would be significant for not only expanding basic properties of the CaCO3 family but also understanding the further application of calcium carbonate hydrates in the future, such as biomineralization, geology, and industrial processes.

**Conflict of interests**

The authors declare no potential conflict of interest.

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**Supporting Information**.

Additional calculated information including Mulliken’s overlap bond population and anisotropic elastic properties.

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**Figures caption**

Fig. 1. The crystal structure of calcium carbonate hydrates;(a) CaCO3·1/2H2O; (b) CaCO3·6H2O; (c) CaCO3·H2O; (d) The calculated X-ray diffraction of calcium carbonate hydrates, (e) the calculated X-ray diffraction of CaCO3·1/2H2O and experimental values by Z.Y. Zou et al[8]

Fig. 2. Phonon dispersion of calcium carbonate hydrates; (a) (b) CaCO3·1/2H2O; (c) (d) CaCO3·6H2O; (e) (f) CaCO3·H2O, the green hollow dots represent experimental values by Z.Y. Zou et al [8]

Fig. 3. Band structure and partial density of states of calcium carbonate hydrates; (a) (b) CaCO3·1/2H2O; (c) (d) CaCO3·6H2O; (e) (f) CaCO3·H2O

Fig. 4. The electric density distribution (a), (c) and (e) and differences of charge density distribution; (b), (d) and (f) for calcium carbonate hydrates on the (100) plane; top: CaCO3·H2O; middle: CaCO3·6H2O; bottom: CaCO3·1/2H2O

Fig.5. The optical properties of calcium carbonate hydrates; (a) Dielectric function; (b) Reflectivity; (c) Conductivity; (d)Absorption; (e) Refractive index; (f) Loss function.

Fig. 6. Contour plots of the Young’s modulus of calcium carbonate hydrates in 3D space. (a) CaCO3·1/2H2O; (b) CaCO3·6H2O; (c) CaCO3·H2O; (d) Planar projections of the Young’s modulus of calcium carbonate hydrates on the (001), (e) (110) crystallographic planes.

Figure S1. The calculated Mulliken's overlap population of calcium carbonate hydrates.

(a) CaCO3·1/2H2O; (b) CaCO3·6H2O; (c) CaCO3·H2O.

Fig S2.The calculated (a) average bond length ((Å)) and (b) the mean bond population ((e)) of calcium carbonate hydrates

Fig. S3. The variations of the elastic moduli (Bulk (*B*), Shear (*G*) and Young moduli (*E*)) value and Poisson’s ratio of calcium carbonate hydrates with different volume.