



Predicted Crystal Structures, Analysis, Impact Sensitivities and Morphology of Solid High-Energy Complexes: Alkaline-Earth Carbohydrazide Perchlorates

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Abstract: The crystal structures, density of states, energy gap, thermodynamic properties, impact sensitivities and morphology of beryllium carbohydrazide perchlorate ($[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$), magnesium carbohydrazide perchlorate ($[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$), calcium carbohydrazide perchlorate ($[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$), strontium carbohydrazide perchlorate ($[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$) and barium carbohydrazide perchlorate ($[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$) were investigated using the density functional theory (DFT) and crystal morphology theory. The results show that all of the complexes have six-coordinated distorted octahedra, which is different from previous works. This was rationalised by consideration of the intermolecular interactions in the crystal structures. Hence the crystal structure is now more reliable. The chemical reactions of the whole molecule may be triggered by an electron transition of CHZ or ClO_4^- . Furthermore the energy gaps were observed, and the values of the impact sensitivities were inferred to have the following sequence: $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$. In addition, the thermodynamic equations at 25-1000 K were obtained. The positive values of the standard molar free enthalpies shows that carbohydrazide perchlorates are stable at 298.15 K. The (1 0 -1) and (0 0 2) faces are the most important growth directions of the crystal morphologies, and have the minimum growth rates. From the cleaved main growth faces, it can be deduced that surface active agents with active hydrogen atoms in the functional groups could be used as crystal-control reagents

to control the crystal morphology for alkaline-earth carbohydrazide perchlorates.

Keyword: crystal structure, density of state, thermodynamic property, impact sensitivity, crystal morphology

1 Introduction

As energetic materials, inorganic coordination compounds with oxidizing species and a metal atom have attracted considerable attention, because of their excellent performance, such as high energy, good stability and so on [1-3]. Carbohydrazide (CHZ, $\text{NH}_2\text{NHCONHNH}_2$) is a good, nitrogen-rich ligand, which can provide several lone-pair electrons to coordinate with the central metal cation [4-7]. Transition metal perchlorate complexes with CHZ, as high-energy and green energetic primary explosives, have been widely studied. In particular the synthesis, molecular structure, and thermal decomposition mechanism of zinc carbohydrazide perchlorate (ZCP) and cadmium carbohydrazide perchlorate (CCP) [8-10] have been studied, and the properties of other metal carbohydrazide perchlorates have been extensively studied experimentally and theoretically.

At the same time energetic materials with alkaline-earth metals have aroused much interest. Energetic alkaline-earth metal carbohydrazide complexes with the nitrate ion [11-13], styphnate ion [14-16] and 3-nitro-1,2,4-triazol-5-onate ion [17] have been studied in detail. Akiyoshi *et al.* [18] studied the influence of the central metal atom on the thermal decomposition behaviour, and found that the alkaline-earth carbohydrazide nitrates are more stable than transition carbohydrazide nitrates. Subsequently, it was deduced that alkaline-earth carbohydrazide perchlorates perhaps have better stability than transition carbohydrazide perchlorates [6, 11]. In 2009, Huang *et al.* [19] investigated the molecular geometries, electronic structures and stabilities of alkaline metal CHZ perchlorates in the gas phase using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid density functional. Their results showed that the Be and Mg complexes were six-coordinated octahedra, the same as the transition metal complexes, but the Ca, Sr and Ba complexes have additional coordinated oxygen atoms from the perchlorate ion. In 2012, Li *et al.* [20] synthesized crystals of Mg carbohydrazide perchlorate, and found that its critical temperature of thermal explosion (T_b) is obviously higher than that for diazodinitrophenel (DDNP) (185 °C) [21-23]. Therefore, it is interesting to predict the crystal structures, thermodynamic properties and impact sensitivities of these. Until now, there have been no reports of the crystal structures of carbohydrazide perchlorates with

the alkaline-earth metal atoms Be, Ca, Sr and Ba in the solid phase.

The shape or morphology of a crystal is extremely important for energetic materials. It has enormous impact on the physical and chemical properties, such as fluidity, apparent density, electrostatic accumulation, pressure resistance, stability, and so on [24, 25]. These properties directly affect the initiating ability, sensitivity and other explosive performance characteristics. For example, it is well known that the acicular crystal of lead azide (LA) is poorer for fluidity and stability, and has higher sensitivity than the columnar crystal form [26, 27]. That is to say, excellent crystal morphology can improve the safety and stability of the energetic material. This is helpful for industrial production and for safe application [28-30]. Therefore, the study of the crystal morphology is vital for energetic materials.

In this work, we have used the density functional theory (DFT) to study the crystal structure, density of states, energy gap, and thermodynamic properties of beryllium carbohydrazide perchlorate ($[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$), magnesium carbohydrazide perchlorate ($[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$), calcium carbohydrazide perchlorate ($[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$), strontium carbohydrazide perchlorate ($[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$) and barium carbohydrazide perchlorate ($[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$), and then predicted the impact sensitivities of them. In addition, the crystal morphologies and their crystal cleavage faces were simulated using MORPHOLOGY code.

2 Computational Method

The calculations were performed within the framework of the density functional theory (DFT) using the CASTEP package [31]. Electron-ion interactions were described by Vanderbilt-type ultrasoft pseudopotentials [32] and orbitals were expanded in a plane-wave basis set. The electronic wave functions were obtained by a density mixing scheme [33] and the structures were relaxed by the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method [31].

The initial configurations of $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$ were designed, according to the experimental data from $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$ using the X-ray single crystal diffraction method [20]. There were four molecules per unit cell. Two different functionals (LDA and GGA) were applied to $[\text{Zn}(\text{CHZ})_3](\text{ClO}_4)_2$ as a test, and the calculated bond lengths and bond angles are given in the Supplementary Material, together with their experimental values from X-ray single crystal diffraction. We found that the GGA (PW91) proposed by Perdew and Wang [34, 35], may be more reliable for predicting the structures of carbohydrazide

perchlorates. Therefore GGA (PW91) was used in all calculations. For the calculation, the cut-off energy was 300.0 eV on the plane wave. The k -point grid was set as $2 \times 2 \times 1$ in the Brillouin zone by using the Monkhost-Pack scheme. The convergence of the total energies was less than 0.01% under the selected kinetic energy and the k -point grid. During the self-consistent field (SCF) calculations, the convergence tolerance of the energy was set to 2.0×10^{-6} eV, the maximum of the residual force was 0.05 eV/Å, the maximum displacement of atoms was 0.002 Å, and the maximum residual bulk stress was 0.1 GPa. The optimized crystal structures were used as the starting point for the morphology calculations.

The morphology of the crystal structures of these complexes was studied using MORPHOLOGY code. The Bravais-Freidel-Donnay-Harker (BFDH) and the growth morphology method were used to predict the crystal growth in a vacuum. The BFDH method was based on the interplanar spacings of the different crystal faces, and took into account the crystal symmetry [36-38]. The growth morphology (AE model) was based on the intermolecular forces in crystallization by Hartman and Perdok [39].

The attachment energy (E_{att}) was defined as the energy per molecule released when a new slice of depth d_{hkl} is attached to the crystal face [40]. It is the sum of the interaction energies per molecule ($E_i(hkl)$) between a slice of thickness d_{hkl} and the i^{th} underlying slice.

$$E_{att} = \sum_{i=1}^{\infty} E_i(hkl) \quad (1)$$

The relationship between the lattice energy of the crystal (E_{latt}) and the energy of a growth slice of thickness d_{hkl} (E_{slice}) is given by:

$$E_{att} = E_{latt} - E_{slice} \quad (2)$$

The relative growth rate (R_{ij}) of the crystal face is proportional to its attachment energy (E_{att}) [41]. The faces with the lowest attachment energies are the slowest growing, and the most important to the morphology.

3 Results and Discussion

3.1 Crystal structures

We set up the crystal structures of $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$, according to the experimental values

of $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$ determined by X-ray single crystal diffraction [20], and then optimized them with DFT. The space group of the five complexes is $P2_1/n$. There are four molecules in the unit cell. All of them have no imaginary vibration frequency because of their C_1 symmetry and energetic minima. The optimized molecular structures and their crystal structures are shown in Figures 1 and 2.

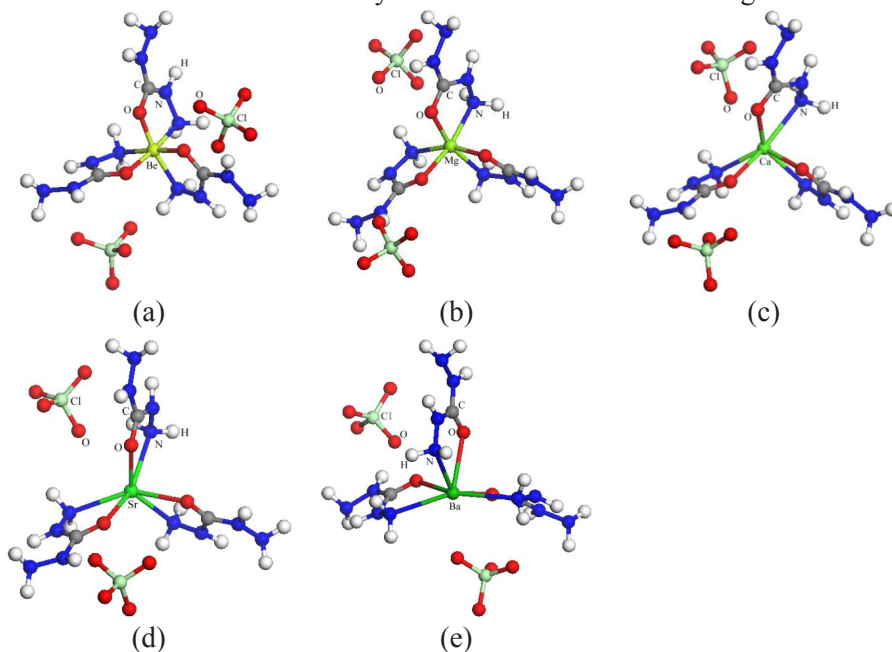


Figure 1. Optimized molecular structures of (a) $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, (b) $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, (c) $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, (d) $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and (e) $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$.

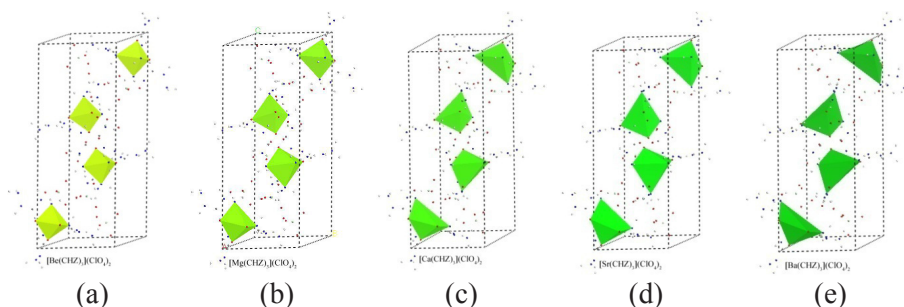


Figure 2. Optimized crystal structures of (a) $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, (b) $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, (c) $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, (d) $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and (e) $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$.

In the crystalline alkaline-earth carbonylhydrazide perchlorates, the metal cation is coordinated with three CHZ groups through the nitrogen atom of the amino group and the oxygen atom of the carbonyl group, forming hexa coordination, distorted octahedra. However, a previous study had shown that, for $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$, in addition to three coordinated carbonylhydrazide molecules, the Ca^{2+} ion coordinates with one oxygen atom of one perchlorate ion, and the Sr^{2+} and Ba^{2+} ions coordinate with two additional oxygen atoms from two perchlorate ions, using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional [19]. This previous work had predicted a single geometric structure under gas phase conditions, and had not considered intermolecular interactions. In their work, the crystal structures contained four molecules in the unit cell. The four molecules interacted, and then attracted outer perchlorate ions to each other. Therefore, it can be seen that the distance between M and O of the perchlorate ion in the crystal structure is obviously larger than that obtained from the molecular structures in Table 1. The distance of M-O (in the perchlorate ions) is too long to form coordination bonds. That is to say, the metal cation is not coordinated to the oxygen atom of the perchlorate ions.

Table 1. The minimum bond lengths (Å) of M-O (in the perchlorate ions) for alkaline-earth carbonylhydrazide perchlorates

	M ^a -O (Molecule) [19]	M-O (Crystal)
$[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$	ionic bond	4.108
$[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$ [20]	--	3.775
$[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$	2.513	2.883
$[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$	2.665	3.526
$[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$	coordination bond	2.864

^a is the central metal.

Table 2 presents the averaged values of the selected calculated bond lengths and bond angles for the alkaline-earth carbonylhydrazide perchlorates. Here we can see that, as the atomic number of the central metal increases, the bond lengths of M-N and M-O increase, whilst the bond angle of N-M-O decreases. This tendency is characteristic of CHZ complexes forming five-membered rings [42]. Table 2 shows that the length of M-N is longer than that of M-O, which indicates that the interaction between M and O is stronger than that between M and N.

Table 2. The averaged values of bond lengths (Å) and bond angles (°) for alkaline-earth carbohydrazide perchlorates

	M ^a -N	M-O	N-M-O
[Be(CHZ) ₃](ClO ₄) ₂	2.031	1.806	83.971
[Mg(CHZ) ₃](ClO ₄) ₂ [20]	2.233	2.028	76.677
[Ca(CHZ) ₃](ClO ₄) ₂	2.564	2.457	65.870
[Sr(CHZ) ₃](ClO ₄) ₂	2.669	2.551	63.730
[Ba(CHZ) ₃](ClO ₄) ₂	2.846	2.678	60.262

^a the central metal.

3.2 Density of states

The density of states (DOS) and partial density of state (PDOS) for [Be(CHZ)₃](ClO₄)₂, [Mg(CHZ)₃](ClO₄)₂, [Ca(CHZ)₃](ClO₄)₂, [Sr(CHZ)₃](ClO₄)₂ and [Ba(CHZ)₃](ClO₄)₂ are presented in Figure 3. Here it can be seen that DOS and PDOS of the five complexes are all very similar. This is due to their similar molecular structures, except for the central metal cations. The valence bands near the Fermi level in DOS are supplemented by the electrons of p orbitals from CHZ and ClO₄⁻. Therefore, it can be deduced that chemical reaction of the whole molecule may be triggered by electron transitions of CHZ or ClO₄⁻.

In the DOS and PDOS of [Be(CHZ)₃](ClO₄)₂ and [Mg(CHZ)₃](ClO₄)₂, the electrons of the s and p orbitals from the metal cation also make a contribution to the valence band near the Fermi level, in addition to those from CHZ and ClO₄⁻. At the same time, the p orbitals between CHZ and Be²⁺ near the Fermi level overlap. According to the maximum overlapping principle, it can be deduced that there is a covalent coordination bond between them, and the bond is the active site for reaction. In the DOS and PDOS of [Ca(CHZ)₃](ClO₄)₂, [Sr(CHZ)₃](ClO₄)₂ and [Ba(CHZ)₃](ClO₄)₂, the overlap of the energy bands between Ca²⁺/Sr²⁺/Ba²⁺ and CHZ are very small, and far from the Fermi level. This indicates that their bonds are very weak, and similar to electrovalent bonds. Hence, we can conclude that the active sites for reaction of these three complexes are ClO₄⁻. This result conforms to the change rule of chemical properties: with the increasing of atomic number, the metallic quality of the atom becomes stronger, and easier to form ionic bonds with others.

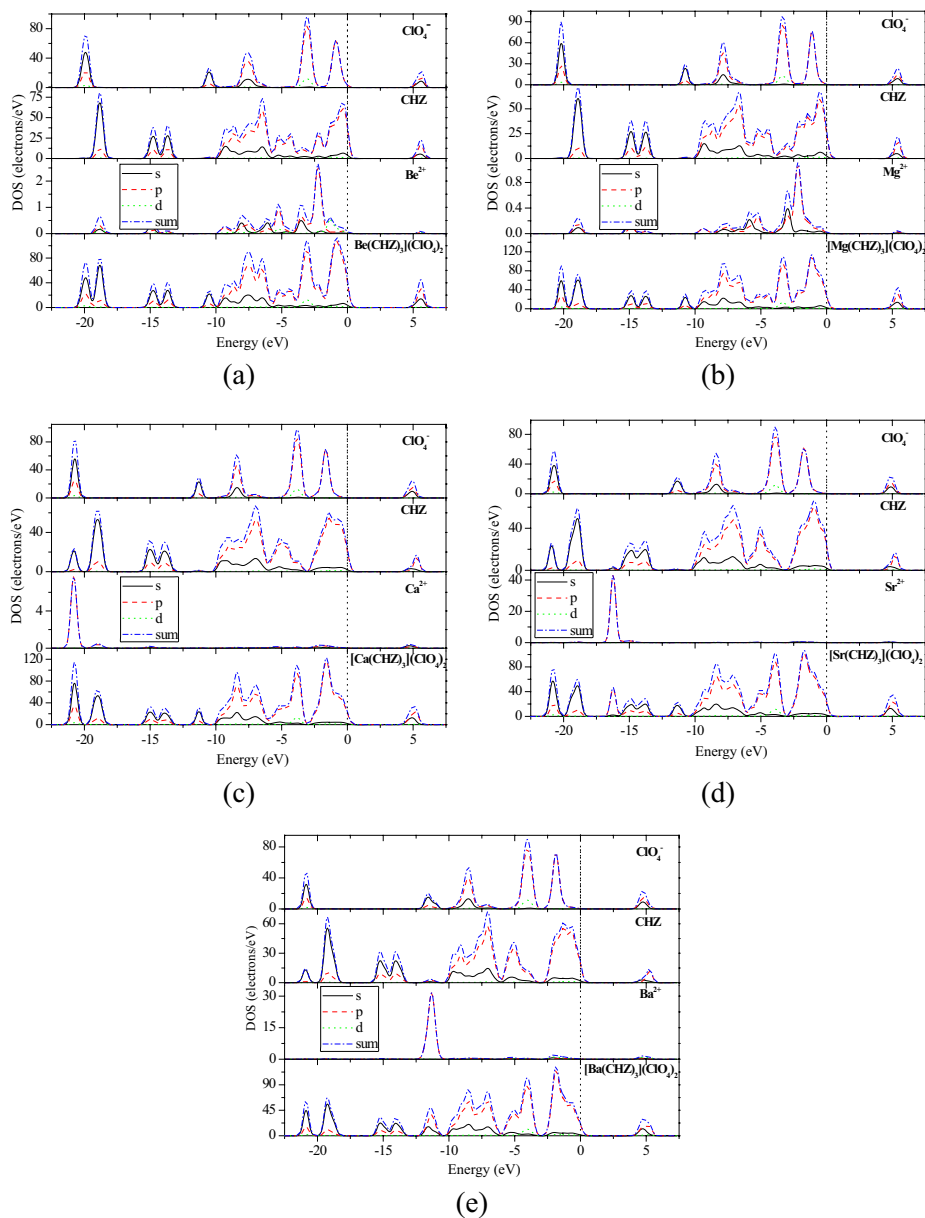
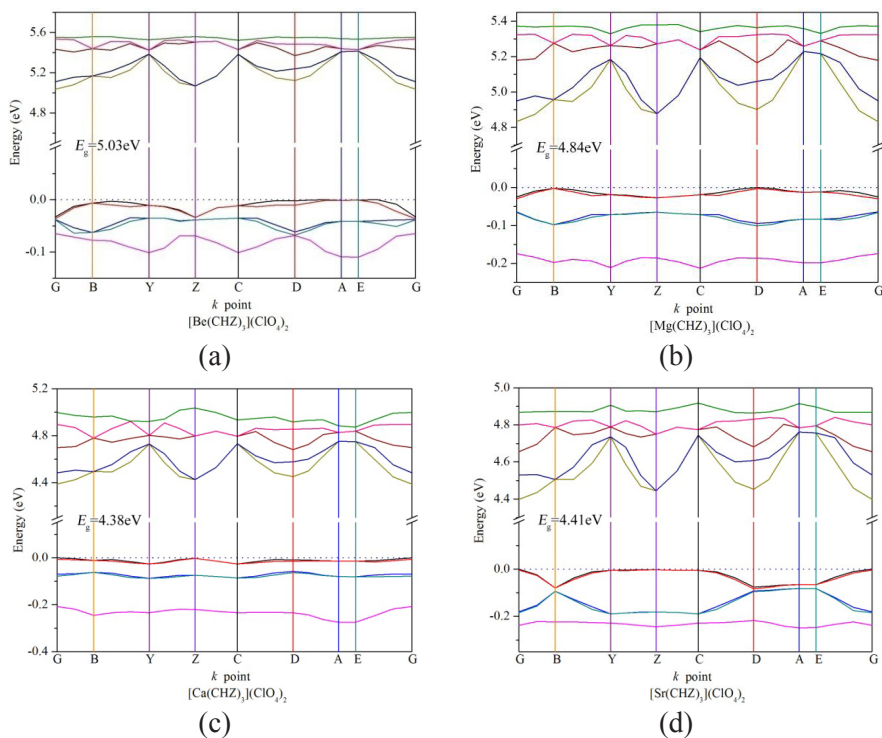


Figure 3. The density of states (DOS) and local density of state (PDOS) for alkaline-earth carbohydrazide perchlorates, (a) $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, (b) $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, (c) $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, (d) $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and (e) $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$.

3.3 Energy gap with impact sensitivity

The energy gap (ΔE) is the energy difference between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), which is an important parameter for characterizing the electronic structures of molecules. The energy gaps of $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$ are listed in Figure 4. It can be seen that the energy gaps of the five complexes are all more than 4 eV. That is to say, they are insulators. A metal atom with a larger atomic number has more positive charge, and is easier to bond electrons. Thus, from Figure 4, it can be seen that the energy gaps are in the following sequence: $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$. Except for $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, the energy gap decreases with increasing atomic number of the central metal cation.



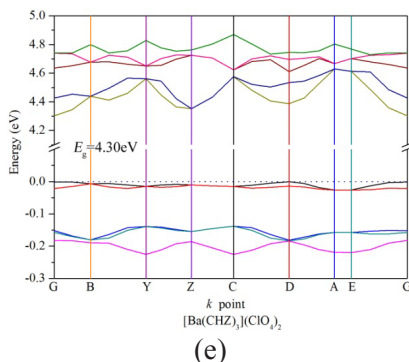


Figure 4. Energy gap (E) of alkaline-earth metallic carbohydrazide perchlorates, (a) $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, (b) $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, (c) $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, (d) $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and (e) $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$.

It is widely known that the energy gap is closely related with some molecular properties. Previous investigations have shown that there is a reasonable relationship between the energy gap and impact sensitivity. According to the principle of the easiest transition, energetic materials with smaller energy gaps are easier to transfer electrons, and are more sensitive to impact [43-46]. That is to say, the smaller the energy gap is, the lower the value of the impact sensitivity ($h_{50\%}$) becomes. Therefore, we can infer that the values of impact sensitivity are in the following sequence: $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$ being the most sensitive of the alkaline-earth metallic carbohydrazide perchlorates.

3.4 Thermodynamic properties

In order to examine the thermodynamic properties of $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$, the standard molar entropy (S_m^0), the standard molar heat capacity ($C_{p,m}^0$), the standard molar enthalpy (H_m^0), and the standard molar free enthalpy (G_m^0) of these complexes were calculated using the vibration frequency, based on statistical thermodynamics [47]. The formulae for these functions are shown in Table 3. From these formulae, the thermodynamic values at different temperature can be calculated.

Table 3. The thermodynamic functions of alkaline-earth metallic carbohydrazide perchlorates at 25-1000 K

	Functions	R ²
[Be(CHZ) ₃](ClO ₄) ₂	$S_m^0 = -0.57244 + 2.12494T - 7.13577 \times 10^{-4} T^2$	0.9994
	$C_{p,m}^0 = 65.41497 + 1.6463T - 8.48796 \times 10^{-4} T^2$	0.9957
	$H_m^0 = 821.63722 + 2.10803T + 3.73879 \times 10^{-4} T^2$	0.9992
	$G_m^0 = 844.25964 - 0.016049T - 6.8773 \times 10^{-4} T^2$	0.9997
[Mg(CHZ) ₃](ClO ₄) ₂	$S_m^0 = -16.13842 + 2.12927T - 7.15597 \times 10^{-4} T^2$	0.9995
	$C_{p,m}^0 = 63.335 + 1.66097T - 8.63004 \times 10^{-4} T^2$	0.9947
	$H_m^0 = 820.99974 + 0.26299T + 3.72479 \times 10^{-4} T^2$	0.9992
	$G_m^0 = 857.35101 - 0.14495T - 6.89262 \times 10^{-4} T^2$	0.9997
[Ca(CHZ) ₃](ClO ₄) ₂	$S_m^0 = -16.49967 + 2.13554T - 7.20237 \times 10^{-4} T^2$	0.9995
	$C_{p,m}^0 = 64.08874 + 1.66141T - 8.65019 \times 10^{-4} T^2$	0.9944
	$H_m^0 = 821.24348 + 0.26474T + 3.71086 \times 10^{-4} T^2$	0.9992
	$G_m^0 = 857.83348 - 0.1456T - 6.89986 \times 10^{-4} T^2$	0.9997
[Sr(CHZ) ₃](ClO ₄) ₂	$S_m^0 = -5.25569 + 2.13945T - 7.28916 \times 10^{-4} T^2$	0.9994
	$C_{p,m}^0 = 68.08647 + 1.63837T - 8.50989 \times 10^{-4} T^2$	0.9946
	$H_m^0 = 820.91739 + 0.26518T + 3.67337 \times 10^{-4} T^2$	0.9992
	$G_m^0 = 857.58058 - 0.15947T - 6.8672 \times 10^{-4} T^2$	0.9997
[Ba(CHZ) ₃](ClO ₄) ₂	$S_m^0 = -14.5421 + 2.12012T - 7.15648 \times 10^{-4} T^2$	0.9995
	$C_{p,m}^0 = 63.82628 + 1.64847T - 8.59085 \times 10^{-4} T^2$	0.9943
	$H_m^0 = 818.91473 + 0.26318T + 3.67691 \times 10^{-4} T^2$	0.9992
	$G_m^0 = 855.28779 - 0.14649T - 6.84716 \times 10^{-4} T^2$	0.9997

where T is the temperature, K; S_m^0 is the equation for the standard molar entropy, $J \cdot mol^{-1} \cdot K^{-1}$; $C_{p,m}^0$ is the standard molar heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$; H_m^0 is the standard molar enthalpy, $J \cdot mol^{-1}$; G_m^0 is the standard molar free enthalpy, $J \cdot mol^{-1}$.

The standard molar free enthalpies (G_m^0) of [Be(CHZ)₃](ClO₄)₂, [Mg(CHZ)₃](ClO₄)₂, [Ca(CHZ)₃](ClO₄)₂, [Sr(CHZ)₃](ClO₄)₂ and [Ba(CHZ)₃](ClO₄)₂ at 25 °C were calculated as follows: 778.34, 752.86, 753.09, 748.99 and 750.75 $J \cdot mol^{-1}$ respectively. The values are all positive, which means that chemical reactions of the five complexes are not spontaneous. They are stable at 25 °C.

3.5 Crystal morphology

The morphology of transition carbohydrazide perchlorate complexes, predicted using the BFDH and AE models in a vacuum, is shown in Figure 5. It can be

symmetrical crystal-faces, and the percent of these three faces occupying the total crystal-surface area is almost 90%. Hence, we can deduce that the faces of crystal growth for the homologous complexes are similar.

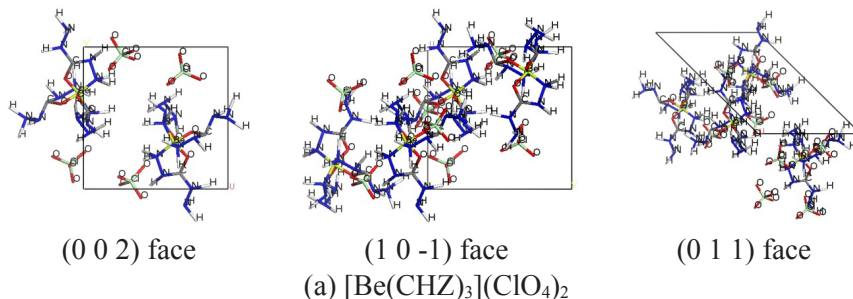
According to the attachment energy, the probable non-bonded energetic interactions during crystal growth can be accounted for [48]. With a more negative attachment energy in a particular direction, the growth rate of the crystal in that direction is faster, and the crystal face bounding the growth direction is less morphologically important [49]. In Table 4, the minimum attachment energies of transition carbonylhydrazide perchlorate complexes are all on the (1 0 -1) or (0 0 2) face. The relative growth rates (R_{ij}) of different crystal faces were also calculated and are listed in Table 4. The growth rates of the (1 0 -1) and (0 0 2) faces are minimum. So it can be deduced that the (1 0 -1) and (0 0 2) faces are the most important growth directions for alkaline-earth carbonylhydrazide perchlorate complexes.

Table 4. Predicted morphologies from the BFDH and AE models for alkaline-earth carbonylhydrazide perchlorate complexes

Complex	Face	BFDH [%]	AE [%]	E_{att} [kcal/mol]	R_{ij}
[Be(CHZ) ₃](ClO ₄) ₂	(1 0 -1)	32.151	32.304	-31.235	1.000
	(0 0 2)	28.967	21.895	-36.788	1.178
	(0 1 1)	31.638	31.454	-44.754	1.433
	(1 0 -3)	3.897	7.914	-41.754	1.337
	(1 0 1)	--	3.224	-42.940	1.375
	(1 1 -1)	2.304	3.192	-51.197	1.639
	(1 1 -2)	1.044	0.016	-55.340	1.772
[Mg(CHZ) ₃](ClO ₄) ₂	(0 0 2)	28.967	21.944	-36.997	1.000
	(1 0 -1)	32.151	32.212	-31.512	0.852
	(0 1 1)	31.638	31.447	-45.055	1.218
	(1 0 -3)	3.897	7.932	-42.037	1.136
	(1 0 1)	--	3.227	-43.247	1.169
	(1 1 -1)	2.304	3.220	-51.557	1.394
	(1 1 -2)	1.044	0.019	-55.742	1.507
[Ca(CHZ) ₃](ClO ₄) ₂	(1 0 -1)	32.151	31.925	-32.391	1.000
	(0 0 2)	28.967	22.095	-37.657	1.163
	(0 1 1)	31.638	31.422	-46.005	1.420
	(1 0 -3)	3.897	7.992	-42.933	1.325
	(1 0 1)	--	3.233	-44.221	1.365
	(1 1 -1)	2.304	3.308	-52.696	1.627
	(1 1 -2)	1.044	0.025	-57.014	1.760

Complex	Face	BFDH [%]	AE [%]	E_{att} [kcal/mol]	R_{ij}
[Sr(CHZ) ₃](ClO ₄) ₂	(1 0 -1)	32.151	31.806	-32.761	1.000
	(0 0 2)	28.967	22.157	-37.935	1.158
	(0 1 1)	31.638	31.411	-46.404	1.416
	(1 0 -3)	3.897	8.020	-43.307	1.322
	(1 0 1)	--	3.233	-44.632	1.362
	(1 1 -1)	2.304	3.346	-53.173	1.623
	(1 1 -2)	1.044	0.027	-57.546	1.757
[Ba(CHZ) ₃](ClO ₄) ₂	(1 0 -1)	32.151	31.606	-33.406	1.000
	(0 0 2)	28.967	22.263	-38.416	1.150
	(0 1 1)	31.638	31.393	-47.098	1.410
	(1 0 -3)	3.897	8.064	-43.960	1.316
	(1 0 1)	--	3.234	-45.347	1.357
	(1 1 -1)	2.304	3.409	-54.006	1.617
	(1 1 -2)	1.044	0.031	-58.475	1.750

Taking the BFDH and AE models into consideration, the cleaved main growth face, (1 0 -1), (0 0 2) and (0 1 1) faces, from the crystal were determined, and their structures are shown in Figure 6. In those cleaved main growth faces, oxygen atoms from ClO₄⁻ and nitrogen atoms from CHZ all existed in or near the crystal surfaces, and the intermolecular interactions are strong. Hence, we can choose surface active agents containing active hydrogen atoms in the functional groups as crystal-control reagents. The oxygen atoms on the crystal faces can form hydrogen bonds with the hydrogen atoms of the crystal-control reagents, and thus the relative growth rates will be changed. Using this method, the crystal morphology growth would be controlled.



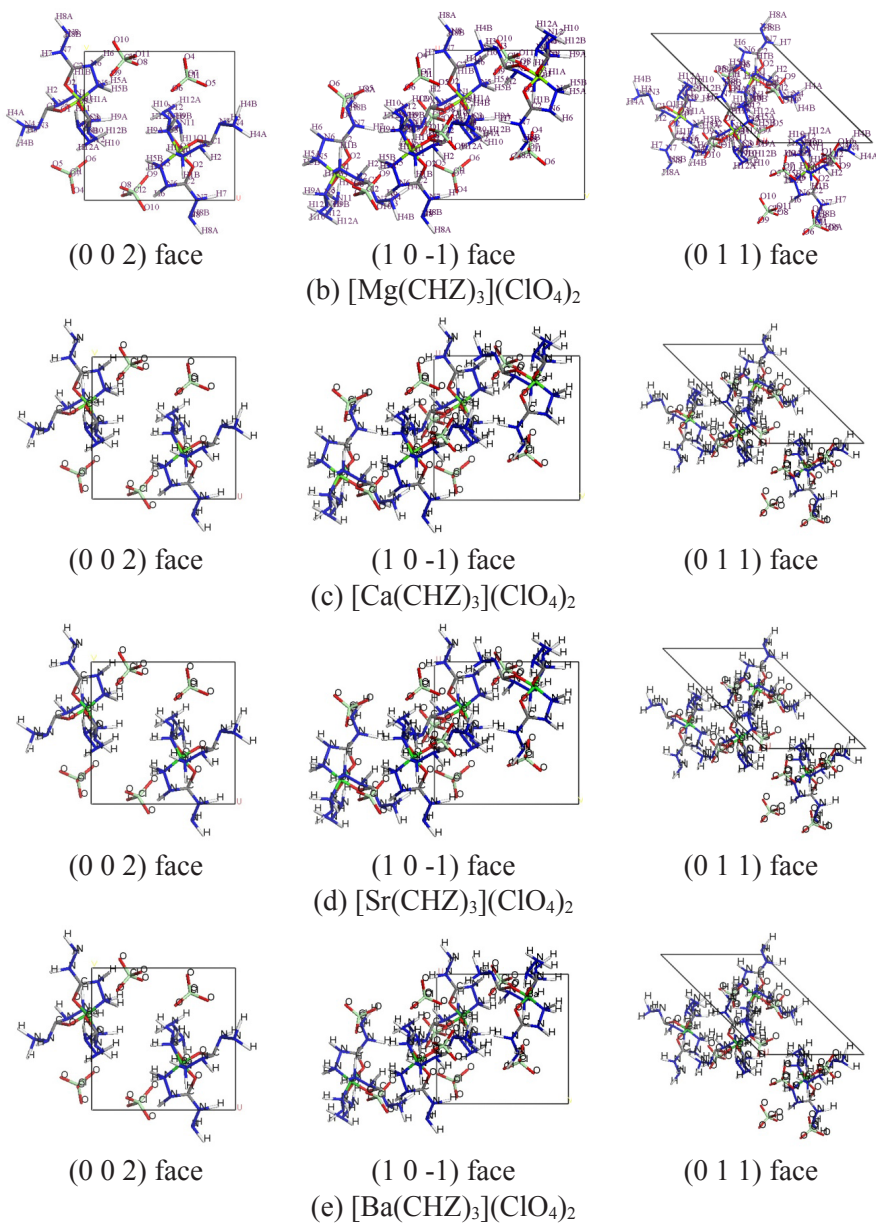


Figure 6. Cleaved main crystal faces of alkaline-earth carbohydrazide perchlorates.

4 Conclusions

The crystal structures of $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$ were studied by DFT. All of the complexes contain distorted, hexa-coordinate octahedra, which can improve the stability of the five complexes. The crystal structures in this work are more reliable than those in previous work, because of the consideration of intermolecular interactions. The interaction between M and O is stronger than that between M and N.

From the DOS and PDOS, it can be deduced that the bond between CHZ and metal cation is the active site for reaction for $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2$, whilst ClO_4^- is the location for $[\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2$, $[\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2$ and $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$. The orders of the energy gaps and the values of the impact sensitivities have the same sequence: $[\text{Be}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Mg}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Sr}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ca}(\text{CHZ})_3](\text{ClO}_4)_2 > [\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$. It was found that $[\text{Ba}(\text{CHZ})_3](\text{ClO}_4)_2$ is the most sensitive of the five. The equations for S_m^0 , $C_{p,m}^0$, H_m^0 and G_m^0 at 25-1000 K were obtained. The positive values of the standard molar free enthalpy shows that carbonylhydrazide perchlorates are stable at 298.15 K.

The crystal morphologies for these are close to oblong blocks, they are mainly formed by the (1 0 -1), (0 0 2) and (0 1 1) faces and their symmetrical crystal-faces. The (1 0 -1) and (0 0 2) faces are the most important growth directions for alkaline-earth carbonylhydrazide perchlorate complexes, because of their minimum growth rates. A surface active agent containing active hydrogen atoms in the functional group could be chosen as a crystal-control reagent, since it could interact with the oxygen atoms on the crystal faces to form hydrogen bonds, achieving the desired control of the crystal morphology.

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