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One-dimensional polymeric carbon structure based on five-membered rings in alkaline earth metal dicarbides BeC_2 and MgC_2

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We studied five alkaline earth dicarbide systems $M_{AE}C_2$ (where M_{AE}=Be-Ba) by using *ab initio* random structure search. For BeC_2 and MgC_2, the lowest energy and dynamically stable configuration consists of five-membered carbon rings connected to each other via an individual carbon atom, stabilized through the donation of electrons from the surrounding alkaline earth ions. For CaC_2, SrC_2, and BaC_2, our study shows that the chain crystal structure is more stable than the predicted structure due to strains induced by the increasing size of alkaline earth metal ions. The reaction energies of the typical synthesis pathway are comparable to those calculated for the experimental reaction of the known chain-type structure. Finally, the proposed structure should be optically distinguishable due to a significantly narrower band gap.

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I. INTRODUCTION

One of the goals for computational materials science is to predict new types of materials and characterize their various properties determined by the electronic structure. In nanotechnology, low-dimensional carbonaceous nanostructures such as graphene, carbon nanotubes, carbon nanoribbons, fullerenes, nanowires, etc., show promising results compared to bulk materials with respect to certain applications.[1–9] For metal dicarbide systems, many extensive studies exist in the literature, e.g., on second-row dicarbides (XC_2, X=Na-Cl),[10–12] transition-metal dicarbides,[13] rare-earth dicarbides,[14] and also alkaline earth dicarbides.[15–21] Most alkaline earth dicarbide systems were found to possess a linear-type crystal structure.[15,16] According to experimental results of the magnesium dicarbide (MgC_2) crystal structure at room temperature, its unit cell is tetragonal with the space group $P4_2/mnm$. C_2 dumbbells are aligned in the perpendicular direction of the tetragonal c axis with C-C bond length of 1.215 Å.[17] For the CaC_2 crystal structure, both experimental and theoretical studies showed that it belongs to the $I4/mmm$ space group.[18,19] The only difference in crystal structure between MgC_2 and CaC_2 is the direction of the C_2 alignment, namely parallel orientation of the C_2 dumbbells to the tetragonal c axis for CaC_2 and perpendicular orientation for MgC_2. X-ray diffraction experiments revealed that the crystal structures of SrC_2 (Ref. 20) and BaC_2 (Ref. 21) at room temperature are analogous to that of CaC_2.

For BeC_2, the ground state structure was so far unknown. Zaleski-Ejgierd *et al.*[22] performed first-principles calculations on both sheet and chain structures and showed that the total energy of the sheet structure is lower than that of the chain structure which was found experimentally for the other alkaline earth dicarbides as described above. However, the harmonic vibrational frequencies at the center of the Brillouin zone (Γ point) of the lowest energy sheet structure show large imaginary frequencies, of the order of $300i$ cm^{-1} and hence the sheet structure appears to be dynamically unstable and is thus ruled out as the correct ground-state crystal structure of BeC_2. In the current work, we carried out an *ab initio* random structure search using density-functional theory (DFT) to identify the ground-state crystal structure of BeC_2. From our search, we found that the lowest energy configuration in BeC_2 resembles a poly[hexadehydro(methyl-cyclopentadiene)] (abbreviated as PH-MCP)-like carbon chain surrounded by Be ions. Applying the same configuration to the MgC_2 system, our results reveal that the total energy of this new crystal structure is actually lower than the chain-type crystal structure of MgC_2 reported from experiments by 0.203 eV/f.u. The lowest energy configuration of MgC_2 systems is thus analogous to BeC_2, i.e., the PH-MCP-like anionic carbon surrounded by Mg ions, whereas chain-type crystal structure reported from experiments is confirmed by us to be more stable than the PH-MCP-like crystal structure for CaC_2, SrC_2, and BaC_2. In the following, we present and discuss the details of our calculations and the obtained results, including structural parameters, total energies, vibrational frequencies, reaction energies, and electronic density of states of the alkaline earth dicarbide systems.

II. COMPUTATIONAL DETAILS

A. *Ab initio* random searching

To search the configurational space we have used a random search method, similar to the *ab initio* random-structure searching method which has been implemented and successfully employed by Pickard and Needs.[23–29] In order to lower the computational cost we have used a structure generation scheme which considers space group symmetries. This results in an efficiency gain which is estimated to be 1 order of magnitude due to the resulting size of the irreducible Brillouin zone. The procedure to create a structure is as follows:

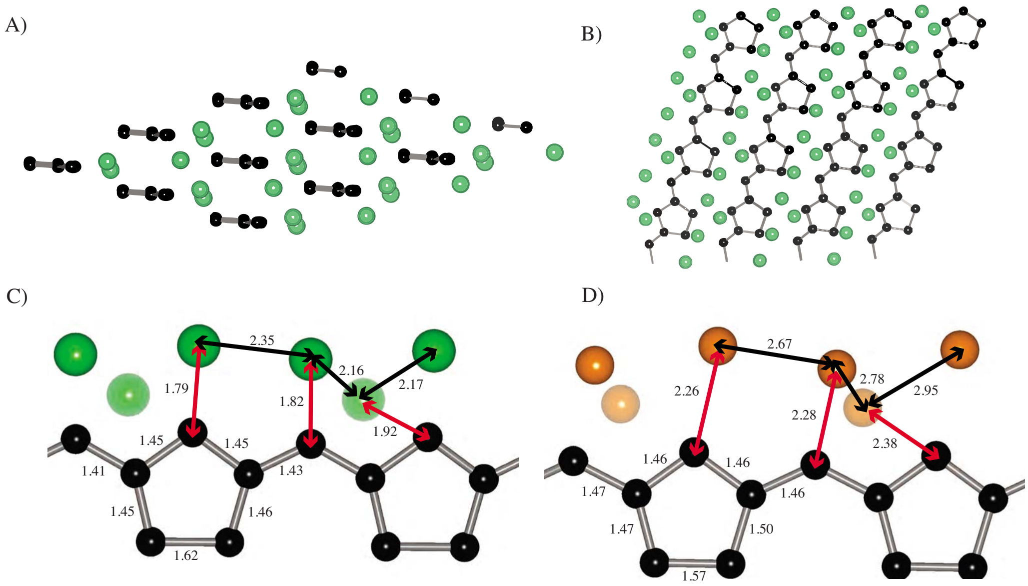

FIG. 1. (Color online) Lowest energy configuration for BeC_2 and MgC_2. The configuration resembles a PH-MCP anionic chain surrounded by alkaline earth metals. (A) Side view. (B) Top view. Light green spheres refer to alkaline earth metals (either Be or Mg) and black spheres represent C atoms. A detailed description of the structure is provided in the text. Structural parameters of the optimized PH-MCP-like crystal structure are shown in (C) for BeC_2 and in (D) for MgC_2. The numbers indicate the bond lengths or distances between pairs of atoms in units of Å. Green spheres in (C) represent Be atoms while orange spheres in (D) represent Mg atoms. C atoms are again drawn in black.

(i) a random space group is selected, (ii) the length of the lattice vectors are randomized, keeping a reasonable volume to get a specific, in this case ambient pressure, (iii) a set of subgroups, and coordinates, are selected randomly to match the stoichiometry of the material, (iv) the structure is allowed to fully relax, and (v) finally the enthalpy of the relaxed structures is compared. For each structure, a **k**-point grid is generated to keep a homogeneous density of **k** points in each direction.

B. *Ab initio* calculations

Total energy and electronic properties of the alkaline earth dicarbide systems were calculated using DFT as implemented in the Vienna *ab initio* simulation package (VASP).[30] Under the projector-augmented wave approach,[31] Perdew, Burke, and Ernzerhof's (PBE) exchange correlation functional[32] was chosen for both alkaline earth metals and carbon. For ionic solids, such as, e.g., sodium alanate ($NaAlH_4$), in which Na donates its charge to the AlH_4 unit, the structural parameters obtained from DFT calculations using the PBE functional were shown to be in excellent agreement with experimental results.[33] In addition, a previous theoretical study of alkaline earth dicarbide systems[22] likewise employed the PBE functional and confirmed that the calculated structural parameters are very accurate in comparison with available experimental data. For the valence states of the alkaline earth metals and carbon, we used 1*s* and 2*s* for Be, 2*p* and 3*s* for Mg, 3*s*, 3*p*, and 4*s* for Ca, 4*s*, 4*p*, and 5*s* for Sr and 5*s*, 5*p*, and 6*s* valence states for Ba, and finally 2*s* and 2*p* valence states for C. The cut-off energy of plane waves and number of **k** points for sampling have been successfully tested for convergence, which yielded 600 eV for the plane-wave expansion and 63 irreducible **k** points generated by the Monkhorst-Pack scheme.[34] The conjugate-gradient algorithm was used for optimizing both the ionic positions and the unit-cell parameters with the forces between the ions determined from the Hellmann-Feynman theorem.

Contribution of dipole-dipole and multipole interactions could be crucially important for an accurate determination of the ground-state energetics in the investigated systems. In this connection, we would like to note that in the self-consistent DFT calculations the total energy is self-consistently calculated until the convergence of the total energy is reached and includes the contributions from the converged charge density. Hence, this energy contains the electrostatic interactions from point charges, dipoles, quadrupoles. etc., from the electron distributions.

III. RESULTS AND DISCUSSION

The random-structure search calculations generated 6535 configurations for BeC_2, from which we found that the lowest energy configuration contains the five-membered ring of the carbon atoms (C_5) connected to a carbon atom forming an infinitely repeated C_5-C-⋯ chain with Be ions trapped along this chain as shown in Fig. 1.

We initially compared our proposed structure to other closely related molecules existing in nature and found that the PH-MCP-like chain somewhat resembles a fully dehydrogenated version of cyclopentene.[35] In cyclopentene (C_5H_8), two carbon atoms in the pentagon ring are connected to a single hydrogen atom and the three other carbons on the ring are terminated with two hydrogen atoms above and below the plane. Moreover, these three carbon atoms pucker by $22° - 28°$.[36] Various experiments[37–39] also revealed that cy-

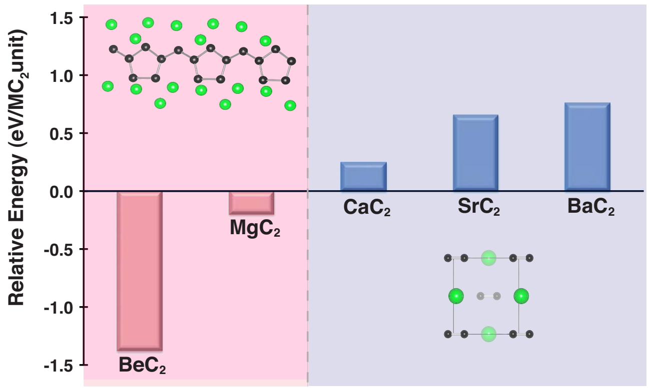

FIG. 2. (Color online) Comparison of energetic stability. The relative energies of alkaline earth dicarbide (per $M_{AE}C_2$ unit) has been calculated as the difference in total energy between the PH-MCP-like structure and the chain structures (Refs. 17–19). The PH-MCP-like chain structure is found to be stable (negative relative energy) for BeC_2 and MgC_2, while for the other alkaline earth dicarbide systems investigated, the chain-type structure is seen to be the favored crystal structure.

clopentene can be polymerized, forming poly(cyclopentene). In our lowest energy configuration, as shown in Fig. 1(A), the alkaline earth metals are trapped in between the PH-MCP-like chains. This is rather similar to the beryllocene (cp_2Be) (cp^-=cyclopentadienyl ion or $C_5H_5^-$) (Refs. 40–43) or ferrocene[44] in which the metal atoms are sandwiched by the cp^- rings.

A. Stability of alkaline earth dicarbide

The chain crystal structure is the generally accepted ground-state configuration for alkaline earth dicarbide systems,[17–19] which prompted us to carry out an energetic comparison with our predicted PH-MCP-like structure. Figure 2 shows the relative energy (calculated as the difference between the total energies per formula unit of the PH-MCP-like structure and the chain crystal structure). A relative-energy value below zero means that the PH-MCP-like structure is energetically more stable than the chain crystal structure, and vice versa, a positive value implies that the chain crystal structure is energetically preferred over the PH-MCP-like structure.

As can be seen in Fig. 2, the PH-MCP-like anionic chain crystal structure is found to be energetically more favorable than the chain crystal structure for both BeC_2 and MgC_2. Moreover, total energies between the crystal structure obtained from the random-search method and all possible sheet structures proposed by Zaleski-Ejgierd *et al.*[22] have been compared by us and we found that our reported crystal structure is significantly lower in energy than any of the sheet structures, by a margin of at least 1.239 eV/MC_2 unit. This shows that the BeC_2 crystal structure proposed by us (Fig. 1) yields a lower energy configuration than both sheet and chain structures. Moreover, we performed an *ab initio* molecular-dynamics simulation (MD) at a simulated temperature of 500 K for a $2\times2\times2$ supercell with a 1 fs time step in order to test if the predicted structure might actually be trapped in a local minimum. Our study revealed virtually no change in the crystal geometry (less than 3% change in structural parameters, e.g., C-C and Be-C bond lengths) after performing 5 ps of the MD simulation, which indicates that the predicted PH-MCP-like structure for BeC_2 can indeed be considerably stable.

The ground state structure of BeC_2 is a trigonal crystal structure with $a=5.480$ Å, $b=4.847$ Å, $c=5.125$ Å, $\alpha=103.3°$, $\beta=144.2°$, and $\gamma=62.7°$. Moreover, the bond length of a C atom connected to the C_5 ring is 1.41 Å, the C-C bond lengths in the five-membered ring are about 1.45 Å, except 1.62 Å for the C-C bond length at the base of the C_5 ring and the Be-C distances range from 1.79 to 1.92 Å. Comparing these structural parameters, in particular the C-C distances of the five-membered with other closely related systems such as beryllocene,[45] $Be(C_5Me_4H)_2(Me=CH_3)$,[46] pyrrole,[47] and cyclopentene,[36] we found that the averaged C-C bond lengths in the five-membered ring obtained by us differs by less than 7% from those other systems. However, the C-C bond at the base of the C_5 ring is rather different, namely 1.62 Å, from our calculation and 1.44 Å, from x-ray diffraction experiment of $Be(C_5Me_4H)_2$.[46] This could be due to C atoms at the base of the five-membered ring in our study being attracted from neighboring Be atoms, resulting in stretching of the C-C bond at the base of C_5 ring. This attractive interaction is absent in $Be(C_5Me_4H)_2$ (Ref. 46) and could thus explain the difference.

To further test the stability of the BeC_2 ground-state crystal structure, the vibrational frequencies at the center of the Brillouin zone (Γ point) of the $2\times2\times2$ BeC_2 supercell were determined by us. This larger cell size leads to a smaller Brillouin zone and makes the vibrational modes at the Γ point more representative of the vibrational modes of the whole system. Our results reveal that BeC_2 in the PH-MCP-like crystal structure possesses only negligibly small imaginary frequencies ($\approx 0.03i$ THz) which can be considered as merely artifacts from numerical inaccuracies.

Based on the results presented for MgC_2 in Fig. 2, the PH-MCP-like anionic chain crystal structure also yields a lower total energy (by about 0.203 eV/MC_2 unit) when compared with the chain crystal structure reported from experiments.[17] The optimized unit cell of MgC_2 is trigonal, as in BeC_2, with lattice constants: $a=5.910$ Å, $b=4.998$ Å, and $c=5.090$ Å, $\alpha=86.4°$, $\beta=132.8°$, and $\gamma=69.3°$. The averaged C-C bond length in the five-membered ring is about 1.46 Å, except 1.57 Å for the C-C bond at the base of the carbon five-membered ring due to an attractive force from Mg ions surrounding the anionic chain. The Mg-C distances are found to vary from 2.26 to 2.38 Å. To confirm the stability of this crystal structure, the vibrational frequencies at the Γ point of the $2\times2\times2$ MgC_2 supercell have been calculated and we found that no imaginary frequencies exist at this point. In principle, these results can be interpreted to imply that the chain crystal structure of MgC_2 as observed in experiments could be merely a metastable state and that its true ground state is actually the predicted PH-MCP-like structure. Obviously, the question arises then why so far only the chain structure has been experimentally observed for MgC_2. We cannot truly answer this question, except putting forward the trivial speculation that a higher reaction barrier might prevent access to the lower energy PH-MCP-like structure. Moreover, we would like to note that the final crystal structure obtained in a synthesis reaction is of course strongly influenced by the choice of reagents. For instance, the chain crystal structure of MgC_2 is found in experiments[17] when a chain-type molecule, namely acetylene (C_2H_2), is used as an initial reagent for synthesis of this alkaline earth dicarbide system. Thus, it is at least conceivable that synthesis of our predicted PH-MCP-like crystal structure might be possible by choosing a five-membered ring molecule, such as cyclopentadienide, as the carbon source in the reagents.

For CaC_2, SrC_2, and BaC_2 (Fig. 2), our results show that the chain-type crystal structure is more favorable configuration, being lower in energy in comparison to our proposed PH-MCP-like crystal structure. These findings are in agreement with what is known experimentally about these compounds.[18,20,21]

As can be seen from the plot in Fig. 2 of the relative energies between the chain and our reported structure, an increase in size of the alkaline earth metal leads to the chain crystal structure becoming more stabilized at the cost of a reduced stability of the PH-MCP-like crystal structure. By considering the size of alkaline earth metal, the Pauling ionic radii of the studied alkaline earth metals with charge +2 follow the trend: $\mathrm{Be}(0.31\ \text{Å}) < \mathrm{Mg}(0.65\ \text{Å}) < \mathrm{Ca}(0.99\ \text{Å}) < \mathrm{Sr}(1.18\ \text{Å}) < \mathrm{Ba}(1.35\ \text{Å})$. The PH-MCP-like crystal structure (Fig. 1) is such that the alkaline earth metals are trapped around the one-dimensional carbon chain and the stability of this structure depends on the donation of a certain amount of electrons from the alkaline earth metals to the carbon chain so that a required negative charge density is achieved in the polymer. However, the number of ions per chain length in the PH-MCP-like structure becomes more and more limited as the ion size increases, leading to difficulties in accommodating larger ions around the chain. As a consequence, the alkaline earth ions start to repel each other (see R1–R3 in Fig. 3) while the system tries to keep the distances between alkaline earth ions and the chain fixed. This competition leads to a lowering of the stability of the PH-MCP-like structure. In addition, the equilibrium distances (S1–S3 in Fig. 3) between alkaline earth ion and the PH-MCP-like chain in alkaline earth dicarbide are found to rise when the ion size increases, leading to a weakening of the electrostatic interaction between the ions and the chains. The stability of the PH-MCP-like crystal structure in $M_{AE}C_2$ is thus reduced when the size of M_{AE} is increasing as seen in Fig. 2 due to a combination of repulsive interaction between each alkaline earth metal and the weakening interaction between chain and M_{AE}.

In the chain crystal structure, the alkaline earth metal is trapped between the C_2 dumbbells. Due to the nature of the crystal structure, it is very easy for large alkaline earth metals to be accommodated in the chain structure. From our results, we measure the C-C distance of the C_2 dumbbell in the chain structure and found that this distance is almost unchanged, namely about 1.27 Å, for all of the chain structures of alkaline earth dicarbide. In addition, the major interaction in the chain structure originates from an attraction between the M_{AE} and C_2 dumbbells while the repulsive interaction between each alkaline earth metal (which is dominating in the PH-MCP-like crystal structure) is very weak due to the rather large separation between adjacent ions. As a result, large alkaline earth metal ions are rather easy to accommodate in the chain structure as opposed to the PH-MCP-like crystal structure and this leads to the observed reduced stability of the PH-MCP-like crystal structure for larger ions as shown in Fig. 2.

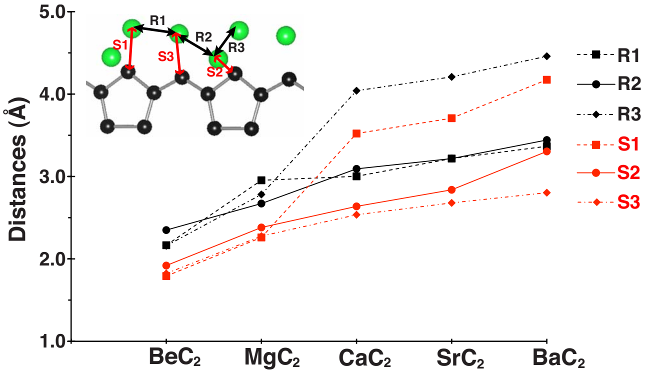

FIG. 3. (Color online) Structural parameters of PH-MCP-like crystal structure in alkaline earth dicarbide. The M_{AE}-M_{AE} and M_{AE}-C(M_{AE}=Be-Ba) distances are represented in black and red lines, respectively. The lines connected between the points are offered only as guide-line to represent the trend of the reported structural parameters. To avoid any ambiguousness of the S2 distances, we would like to note that the S2 distance is slightly larger than the S3 distance because the corresponding Be atoms are trapped at a deeper plane than the carbon chain's layer.

B. Synthesis reaction paths of beryllium and magnesium dicarbide

MgC_2 can be experimentally synthesized by the following reaction:[17]

$$2\mathrm{Mg} + \mathrm{C_2H_2} + \mathrm{O_2} \rightarrow \mathrm{MgC_2} + \mathrm{MgO} + \mathrm{H_2O}.$$

The corresponding reaction energy is calculated by us to be exothermic with −9.294 eV/f.u. The reaction energy of the PH-MCP-like structure for MgC_2 is found to be lower than that of the experimental MgC_2 chain structure, namely, −9.497 eV/f.u. We would like to emphasize that these reaction energies are simply calculated as the difference between total energies of reactants and products, and are not to be confused with reaction enthalpies normally reported from experimental measurements. Based on these results, it appears at least possible that the crystal structure reported by us might be synthesized using the above reaction. However, as remarked previously, the energy barrier to reach the PH-MCP-like crystal structure could be too high, preventing its formation, whereas it might be comparatively low for the case of the chain structure.

For BeC_2, we considered the analogous reaction

$$2\mathrm{Be} + \mathrm{C_2H_2} + \mathrm{O_2} \rightarrow \mathrm{BeC_2} + \mathrm{BeO} + \mathrm{H_2O}.$$

From our calculations, this reaction also exhibits exothermic behavior, releasing 9.765 eV/f.u. in the process, which is comparable in magnitude to the reaction energies of MgC_2. Of course, this is not meant to imply that it will be possible to synthesize the PH-MCP-like crystal structure of BeC_2 according to the above reaction, since for example high reaction barriers could prevent such a pathway. Nevertheless, it is encouraging to obtain a reaction energy which is close in magnitude to that of MgC_2, offering at least in principle the chance (e.g., through selection of a suitable catalyst or proper reactants) that our predicted structure could eventually be synthesized.

Considering the alternative reaction

$$M + \text{graphite} \rightarrow MC_2, \quad \text{where} \quad M = \text{Be} \ \text{or} \ \text{Mg}$$

our results reveal that this reaction is also exothermic but with a much reduced reaction energy of 0.91 eV/f.u. and 1.10 eV/f.u. for M=Be and Mg, respectively. This proposed path of transformation might be another possible synthesis route, but in comparison to the energies calculated by us for the experimental reaction route,[17] the above obtained energies are rather lower. As a consequence, the PH-MCP-like crystal structure of prepared alkaline earth dicarbides might easier decompose into the alkaline earth metal and graphite.

C. Density of states of BeC_2 and MgC_2

According to our results presented in Fig. 2, the lowest energy crystal structure of both BeC_2 and MgC_2 is the PH-MCP-like configuration. Figure 4 shows the calculated total and partial density of states in both systems. It can be clearly seen that $2p$ hybridized states of Be exhibit a larger overlap with C $2p$ states whereas the interaction between Mg and C is rather weak due to less overlap between either $2s$ or $2p$ states of Mg with C $2p$ states near the Fermi level. Consequently, Be is bound more strongly to C than Mg is, leading to shorter interatomic distances between Be and C. This finding is in agreement with our results presented in Fig. 3 where it can be seen that the distance between alkaline earth ions and the carbon atoms of the chain is rising when the ion size is increased. As can be seen in Fig. 4, the band gap in the PH-MCP-like crystal structures is rather narrow, namely, 0.51 eV and 0.60 eV for BeC_2 and MgC_2, respectively. Moreover, we also performed density functional theory calculations with hybrid functions[48] (this approach is generally assumed to lead to higher accuracy in band gap prediction) and found that these band gaps are found to increase by a factor of two. To investigate the band gap of the chain structure MgC_2, our density of states plot reveal that it is an insulator with a wide band gap of about 3 eV. The calculated density of states of the chain MgC_2 crystal structure is in very good agreement with result reported in the literature.[16] The rather large difference in the band gap for these two crystal structures of MgC_2 offers an intriguing possibility for optical distinction in experiments.

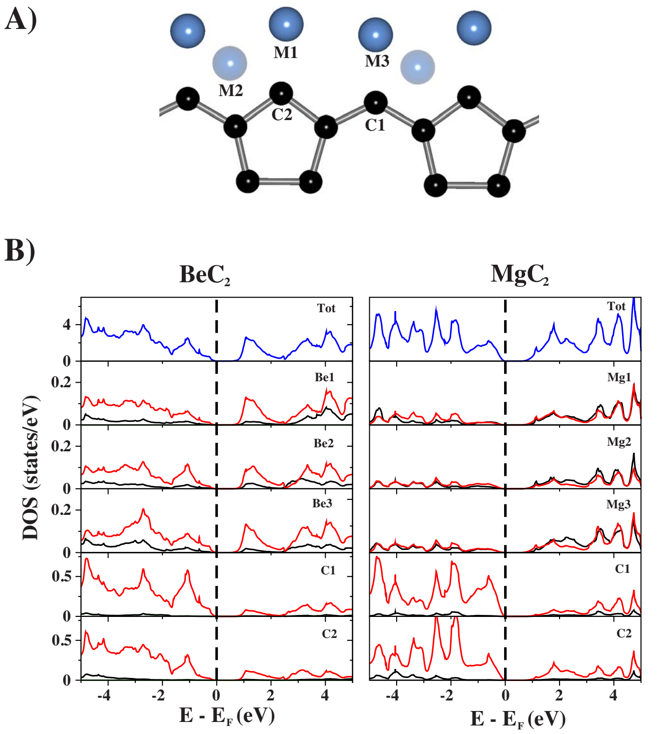

FIG. 4. (Color online) (A) Schematic of the alkaline earth dicarbide structure, indicating labels for the alkaline earth metal and carbon atoms used in the following in the partial density of states plots. M stands for either Be or Mg. (B) Total and partial density of states of the PH-MCP-like BeC_2 and MgC_2 crystal structures. For the density of states (DOS) calculations, the total DOS is denoted by blue lines and the DOS projected onto the s and p atomic orbitals are shown as black and red lines, respectively. Dashed vertical lines indicate the position of the Fermi energy.

IV. CONCLUSIONS

Ab initio random-structure search combined with density-functional theory was used by us to find and study the lowest energy configuration of alkaline earth dicarbide systems. Our results reveal a so far unknown ground-state crystal structure for BeC_2 and MgC_2 which resembles poly[hexadehydro(methyl-cyclopentadiene)] (abbreviated as PH-MCP) anionic chains (i.e., an infinite chain of carbon five-membered ring each connected via a single carbon atom) surrounded by alkaline earth metals. The stability of this structure was confirmed from both total energy and vibrational frequency calculations.

For CaC_2, SrC_2, and BaC_2, the most stable crystal structure is found to be the chain structure, in agreement with what is known experimentally. In addition, we offer an explanation as to why the stability of the PH-MCP-like crystal structure in alkaline earth dicarbide systems is decreasing when the size of alkaline earth metals is growing. This is presumably due to the combination of rising repulsion between each alkaline earth metal and a weakening in the interaction between alkaline earth metal and the PH-MCP-like chain.

From reaction energy calculations, we found that both BeC_2 and MgC_2 might be possible to synthesize by the experimental reaction. Since the crystal structure of the final product obtained in a synthesis reaction is strongly affected by the choice of reagents, it might be possible to prepare our predicted PH-MCP-like crystal structure by including a five-membered carbon ring molecule, such as cyclopentadienide, in the reagents.

Finally, based on the electronic density of states, the electronic band gaps are found to be 0.51 eV and 0.60 eV for the BeC_2 and MgC_2, respectively. These calculated band gaps of the PH-MCP-like structure are rather narrow in comparison to those of the chain structure, which possesses a large band gap of about 3 eV. This feature could be rather useful for an optical distinction between the two structure types.

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