**Density functional theory study on geometries, stability and electronic structures
of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters**

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ABSTRACT

The geometries, stability and electronic structures of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n = 2-10$) clusters have been calculated by density functional theory (DFT) method. The results demonstrate that the Ca atom tends to replace the Mg atom which is surrounded by more O atoms. $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ clusters have slightly higher symmetry than the corresponding $\text{CaMg}_{n-1}\text{O}_n$ clusters. The Ca doping strengthens Mg-O average bond lengths of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ as the cluster size increased. $\text{Ca}_2\text{Mg}_2\text{O}_4$ clusters have higher stability than their neighbors. The chemical reactivity of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters is slightly higher than that of $(\text{MgO})_n$ clusters.

Keywords: A. Nanostructures; C. First-principle Calculations; D. Electrical Properties; D. Microstructures

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1. Introduction

MgO may be the major component of the Earth's lower mantle[1]. MgO nanostructures exhibit extensive applications in catalysis, refractory, paint and superconductor industries[2]. Refractory materials which the main components are MgO and CaO have the strong ability to resist erosion in alkaline slag in metallurgy. However, CaO has the hydrophilic which will decrease the stability of the refractory materials. It is useful to study the dolomite sintering process which can make the CaO surrounded by MgO. A variety of experimental and theoretical researches have been conducted on MgO clusters[2]. The catalytic activity of MgO from the dolomite thermal decomposition is considerably higher than that from magnesite. Accurate control of dolomite thermal decomposition will further improve the reactivity. The thermal decomposition temperature of MgCO_3 in dolomite is lower than that of CaCO_3 in dolomite[3]. Therefore, it would be interesting to know how the properties of small $(\text{MgO})_n$ clusters are affected by doped Ca atom. Ge *et al.*[4] have systematically investigated the geometries and electronic properties of $\text{Fe}(\text{MgO})_n$ by the density functional theory. Wang *et al.*[2] have performed a systematic study on geometries, stability, and electronic structures of the Mn-doped magnesia clusters using DFT calculations. Wu *et al.*[5] have investigated the stable geometries, electronic and magnetic properties of MgO sheets with Mg atom substituted by 3d transition metals (TM) (Mn, Fe, Co, and Ni) by first-principle calculations.

In this work, to compare the activity of the dolomite thermal decomposition products with the magnesite thermal decomposition product, we investigated the geometries, stability, and electronic structures of the local minimum $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters using DFT calculations. The theoretical method and computational details are

described in Section 2. The calculated results are discussed in Section 3. Our findings are summarized in Section 4.

2. Computational details

(MgO)_n clusters are formed firstly and then CaO occurs during the thermal decomposition process of dolomite. So (MgO)_n clusters are considered as the basis. The stable structures of (MgO)_n clusters are referred from Ref.[6-14]. Structures of CaMg_{n-1}O_n clusters are achieved by substituting a Mg atom with a Ca atom in the lowest-energy (MgO)_n clusters. The structures of Ca₂Mg_{n-2}O_n clusters are obtained by further substituting a Mg atom with a Ca atom in the local minimum CaMg_{n-1}O_n clusters. Our calculations are performed using the spin polarized DFT which is implemented to the DMol³ package[15,16]. The exchange-correlation interaction is treated with the generalized gradient approximation (GGA) using the BLYP hybrid exchange functional[17,18]. There are no symmetry constraints on the optimization of (MgO)_n and Ca_mMg_{n-m}O_n (m=1-2, n=2-10) structures[2]. The spin multiplicity is considered to obtain the most favorable spin states[19]. The double numerical polarization (DNP) basis set is adopted[15], core treatment is set to effective core potentials. Müliken population analysis is adopted to obtain the atomic charges of the clusters[20,21].

We adopt the following convergence thresholds for local optimization: total energy convergence tolerance is 1.0×10^{-5} Hartree steps, 2×10^{-3} Hartree/Å for maximum force and 5×10^{-3} Å for maximum displacement. The energy gradient converge to within 1×10^{-5} Hartree/Bohr. In self-consistent functional (SCF) calculation, charge density tolerance is 1.0×10^{-6} e/Å³, smearing is set to 5.0×10^{-5} Hartree. In the structural optimization, vibration frequency are calculated to verify that all the structures are stable.

After the optimization, the structural stability of the local minimum $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters is analyzed by the binding energy. The average binding energy $E_b(n)$ is defined[2,22]

$$E_{b1}(n) = [nE(\text{Mg}) + nE(\text{O}) - E((\text{MgO})_n)] / 2n \quad (1)$$

$$E_{b2}(n) = [(n-1)E(\text{Mg}) + nE(\text{O}) + E(\text{Ca}) - E(\text{CaMg}_{n-1}\text{O}_n)] / 2n \quad (2)$$

$$E_{b3}(n) = [(n-2)E(\text{Mg}) + nE(\text{O}) + 2E(\text{Ca}) - E(\text{Ca}_2\text{Mg}_{n-2}\text{O}_n)] / 2n \quad (3)$$

where $E(\text{Mg})$, $E(\text{O})$ and $E(\text{Ca})$ are the energies of the isolated Mg, O and Ca atoms, respectively. $E((\text{MgO})_n)$, $E(\text{CaMg}_{n-1}\text{O}_n)$ and $E(\text{Ca}_2\text{Mg}_{n-2}\text{O}_n)$ represent the total energies of the lowest-energy structures for the $(\text{MgO})_n$, local minimum structures for the $\text{CaMg}_{n-1}\text{O}_n$ and those for the $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ clusters, respectively. $2n$ represents the cluster size.

The relative stability of these clusters can be better understood by calculating the second-order energy differences[2,23]:

$$\Delta^2 E_1 = E(\text{MgO})_{n+1} + E(\text{MgO})_{n-1} - 2E(\text{MgO})_n \quad (4)$$

$$\Delta^2 E_2 = E(\text{CaMg}_n\text{O}_{n+1}) + E(\text{CaMg}_{n-2}\text{O}_{n-1}) - 2E(\text{CaMg}_{n-1}\text{O}_n) \quad (5)$$

$$\Delta^2 E_3 = E(\text{Ca}_2\text{Mg}_{n-1}\text{O}_{n+1}) + E(\text{Ca}_2\text{Mg}_{n-3}\text{O}_{n-1}) - 2E(\text{Ca}_2\text{Mg}_{n-2}\text{O}_n) \quad (6)$$

where $E(i)$ represents the total energy of the corresponding i system.

3. Results and discussion

3.1. Geometries

$\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) isomers are compared by the binding energy. The optimized lowest-energy $(\text{MgO})_n$ and local minimum $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters and low-lying isomers $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters are shown in Fig.1 and Fig.2, respectively. (Yellow ball: Ca atom, red ball: O atom and lawngreen ball: Mg atom).

Table S1 in supplementary material lists the point group symmetry, binding energy E_b (in eV), the energy E (in eV) of HOMO, the electron occupation number n_e in the HOMO, the on-site charge Q (in e) of the Ca, Mg and O atoms (the number in parentheses is the number of atoms), and spin multiplicity (M_s).

As shown in Fig.1 and Table S1, the $\text{CaMg}_{n-1}\text{O}_n$ ($n=2-10$) clusters have lower symmetry than the corresponding $(\text{MgO})_n$ clusters. $\text{CaMg}_{n-1}\text{O}_n$ ($n=2, 3, 4$ and 6) clusters possess an independent Ca-doped structure, respectively. Structures of $\text{CaMg}_{n-1}\text{O}_n$ ($n=2-4$ and 6) in sequence are a rhombus structure (C_{2v}), a hexagonal ring (C_{2v}), a rhombohedral distortion (C_{3v}), a stacked double ring structure (C_s). The local minimum structure of CaMg_4O_5 is a capped distorted rhombohedron (C_1). Other isomers of CaMg_4O_5 clusters are less stable. The binding energy differences between this capped distorted rhombohedron structure C_1 and the other structures (C_s) are 0.001 eV, 0.120 eV, 0.340eV and 0.378 eV, respectively. The local minimum structure of CaMg_6O_7 is a cage structure (C_s). The other low-lying isomers (C_{3v} and C_s) have slightly higher energy (0.164 eV and 0.392 eV), respectively. For CaMg_7O_8 , the local minimum structure is a hybrid structure (C_1). The energy of the remaining isomer (C_1) is slightly higher (0.166 eV). The local minimum structure of CaMg_8O_9 is a stacked ternary ring structure (C_{2v}). A Mg atom in the inner-layer hexagon of $(\text{MgO})_9$ clusters is replaced by a Ca atom which is different from Mn-doped $(\text{MgO})_9$ [2]. The binding energies of the other isomer (C_s) is 0.012 eV higher than that of the (C_{2v}) structure. The local minimum structure of $\text{CaMg}_9\text{O}_{10}$ is a cage structure (C_1). The other low-lying isomers (C_1) have higher energy (0.088 eV, 0.154 eV, 0.223 eV and 0.314 eV), respectively. In a word, a Ca doping only causes some local structural distortions and the basic geometric configurations of $(\text{MgO})_n$ clusters are kept. It can also be found that the Ca atom is

inclined to replace the Mg atom which is surrounded by more O atoms. It is because that the *d*-polarisation effect of Ca atoms in CaO clusters[24].

As shown in Fig.2, the structures of $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ ($n=2-10$) are similar to those of the corresponding $\text{CaMg}_{n-1}\text{O}_n$ ($n=2-10$) clusters while the $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ clusters have slightly higher symmetry than the corresponding $\text{CaMg}_{n-1}\text{O}_n$ clusters. Aguado *et al.*[25] have pointed out polarization effects were conducive to form surface sites. It implies that it is not feasible to make the CaO surrounded by MgO in sintering process, but the other elements doped may solve the above problem.

3.2. Bond lengths

Size dependence of average bond lengths (R_{mean}) for $(\text{MgO})_n$ ($n=2-10$) clusters and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters is shown in Fig. 3. The average Mg-O bond lengths of $(\text{MgO})_n$ ($n=2-10$) clusters are in the range of 1.851 Å to 2.037 Å. The bond lengths of the considered $(\text{MgO})_n$ clusters are slightly larger than those of $(\text{MgO})_n$ clusters in Ref.[7,10,14]. It can be seen that the average bond lengths of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters are slightly larger than those of $(\text{MgO})_n$ clusters. It is worth considering that the Ca doping strengthens Mg-O average bond lengths of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ as the cluster size increased.

3.3. Stabilities

Size dependence of the average binding energies of $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ is displayed in Fig.4. The calculated binding energies of $(\text{MgO})_n$ clusters with BLYP theory in this study are slightly lower than those with LDA theory[6] but slightly larger than those with BL3YP and 6-311G(d) theory[7]. $(\text{MgO})_6$ and $(\text{MgO})_9$ possess higher stability than other $(\text{MgO})_n$ clusters which have been confirmed by infrared spectra for $(\text{MgO})_{3n}$ ($n = 2-5$)[11] and the mass spectra of magnesia clusters[26]. From Fig. 4 it can

also be seen that $\text{Ca}_2\text{Mg}_2\text{O}_4$ cluster possess higher stability than their neighbors. Previous calculations found that the rocksalt slab shape was preferred to CaO nanoclusters[6,25,27]. Based on packing arguments[7], ion pairs in MgO clusters with larger absolute anion-cation radii differences produce regular hexagonal-ring-based structures, while CaO clusters with smaller absolute anion-cation radii differences prefer slab structures. Obviously the Ca-doped configurations have relatively higher the average binding energies. As the cluster size increased, the binding energy differences between $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ will be decreased due to a decrease in the proportion of Ca and Mg.

Size dependence of the second-order energy differences for the considered $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters is shown in Fig.5. It can be seen that the local peaks of Δ^2E_n curves appear at $n=4, 6$, and 9 , while local valleys of Δ^2E_n curves appear at $n=3, 5$, and 7 [2]. It implies that the stability of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ is agreement with that of $(\text{MgO})_n$ clusters. It also reveals that the same high stability at $n=6$ and 9 . Dong *et al.* [12] found that $(\text{MgO})_6$ and $(\text{MgO})_9$ possess higher stability than their neighbors. It can also be found that the relative structural stability decreases as the Ca atoms are doped.

3.4. Electronic structures

The Mlliken charge distributions of the $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters are listed in Table S1. From Table S1 it can be found that the charges of Ca atoms are more positive than those of Mg atoms in the $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters. Such as the doped Ca atom in $(\text{MgO})_2$ leads to the Mlliken charges of Mg atom changed from $0.941 |e|$ to $0.822 |e|$ and the Mlliken charges of O atoms changed from $-0.941 |e|$ to $-1.086 |e|$. Charges of Ca atoms gradually increase with the cluster size increased. The charge reduction in the small oxide clusters is responsible for a special stability of the diatomic molecule. MgO clusters have a

strong dimerization. While the charge reduction of CaO clusters is less important and dimerization does not occur[25]. The charges of Ca atoms in the $\text{CaMg}_{n-1}\text{O}_n$ clusters changed within the range from 1.350 |e| to 1.465 |e|, and those in the $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ clusters change within the range from 1.249 |e| to 1.465 |e|. From Table S1 it can also be seen that Ca doping does not change the values of spin multiplicities of $(\text{MgO})_n$.

The energy gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $(\text{MgO})_n$ ($n=2-10$) and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ as a function of cluster size are illustrated in Fig. 6. It can be found that the HOMO-LUMO gap for $(\text{MgO})_5$ significantly drops[10]. Detailed orbital analysis for $(\text{MgO})_5$ reveals that they possess lower coordinated atoms, the main contributions in the highest band of the occupied molecular orbital are from Mg $3s$ and $3p$, where these orbitals should be vacant or much less populated in the real electronic state of the MgO solid[10]. The valence band of these clusters is mainly O $2p$ derived[10]. It can also be seen that three peaks occur at $n=3, 6, 9$ for $(\text{MgO})_n$ ($n=2-10$) and $\text{CaMg}_{n-1}\text{O}_n$ clusters while those for $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ are transferred to $n=4, 6, 9$. It can be explained that the electrons in the HOMO of Ca atoms feel a stronger effective core potential since the electron screening is weaker for electrons in the same orbital than that for inner-shell electrons[4]. Malliavin *et al.*[6] have found that the HOMO and the contribution of the $3d$ orbital were very different in the CaO and MgO clusters, leading to a different type of bonding. In general, clusters with larger HOMO-LUMO energy gaps are stable and less chemically reactive. It can be seen that the chemical reactivity of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ is slightly better than that of $(\text{MgO})_n$ clusters. Aguado *et al.*[25] pointed out that polarization effects reduced the stability of highly compact structures containing anions with bulk coordination. It explained that Ca doping improved the catalysis of $(\text{MgO})_n$ clusters.

4. Conclusions

We compared the geometric structures of $(\text{MgO})_n$ ($n=2-10$) with $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ ($m=1-2$, $n=2-10$) clusters by DFT calculations using the BLYP functional in GGA method in the DMol³ package. The results showed that the Ca atom tends to replace the Mg atom which was surrounded by more O atoms. $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ clusters have slightly higher symmetry than the corresponding $\text{CaMg}_{n-1}\text{O}_n$ clusters. The Ca doping strengthened the Mg-O average bond lengths of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters as the cluster size increased. $\text{Ca}_2\text{Mg}_2\text{O}_4$ clusters possessed higher stability than their neighbors. The chemical reactivity of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ was slightly higher than that of $(\text{MgO})_n$ clusters.

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Figure Captions

Fig.1. The lowest-energy $(\text{MgO})_n$ and local minimum $\text{CaMg}_{n-1}\text{O}_n$ clusters and low-lying isomers $\text{CaMg}_{n-1}\text{O}_n$ clusters. (Yellow ball: Ca atom, red ball: O atom and lawngreen

ball: Mg atom)

Fig.2. The local minimum and low-lying isomers $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters. (Yellow ball: Ca atom, red ball: O atom and lawngreen ball: Mg atom)

Table S1. The point group symmetry, binding energies E_b (in eV), the energy E (in eV) of HOMO, the electron occupation number n_e in the HOMO, the on-site charge Q (in e) of the Ca,Mg and O atoms (the number in parentheses is the number of atoms) and spin multiplicities (M_s).

Fig. 3. Size dependence of average bond lengths ($R_{\text{mean}}/\text{\AA}$) for $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters.

Fig. 4. Size dependence of the average binding energies (E_b/atom) for $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters.

Fig. 5. Size dependence of the second-order difference of cluster energies for $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters.

Fig. 6. Size dependence of the HOMO-LUMO gaps for $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters.

Fig 1

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Fig. 6. Size dependence of the HOMO-LUMO gaps for $(\text{MgO})_n$ and $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ clusters.

From Fig. 6 it can be seen that three peaks occur at $n=3, 6, 9$ for $(\text{MgO})_n$ ($n=2-10$) and $\text{CaMg}_{n-1}\text{O}_n$ clusters while those for $\text{Ca}_2\text{Mg}_{n-2}\text{O}_n$ are transferred to $n=4, 6, 9$. It can be explained that the contribution of the $3d$ orbitals are very different in the CaO and MgO clusters. From Fig. 6 it can be seen that the chemical reactivity of $\text{Ca}_m\text{Mg}_{n-m}\text{O}_n$ is slightly better than that of $(\text{MgO})_n$ clusters. Aguado *et al.*[25] pointed out polarization effects reduced the stability of highly compact structures containing anions with bulk coordination. It explained that Ca doping improved the catalysis of $(\text{MgO})_n$ clusters.