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Synthesizing Metastable Rocksalt-Type MgTe Based on High-Pressure Solid-State Phase Transition: A First-Principles Study *

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The controllability of pressure-induced structural transformation in the hexagonal wurtzite-type MgTe is studied by a first-principles pseudopotential method within the generalized gradient approximation (GGA). Based on the transitional mechanisms of the wurtzite→NiAs and the wurtzite→rocksalt, a special method of loading biaxial pressure on the (010) and (001) planes of an orthorhombic cell is designed. At equal biaxial pressure of 2.75 GPa, an abrupt volume collapse is found and the WZ phase transforms into an orthorhombic phase with a tiny distortion. While the pressure decreases to zero, three lattice parameters a, b and c become equal and a metastable rocksalt-type MgTe is obtained.

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The wide-band-gap semiconductor compound MgTe is of great importance due to its potential applications in the field of electro-optic devices.[1,2] Under ambient conditions, MgTe adopts a wurtzite (WZ) structure with a space group $P6_3mc$ or NiAs (NA) structure with space group $P6_3/mmc$, unlike other alkaline-earth (except for beryllium) chalcogenides which crystallize into a rocksalt (RS) structure. Zachariasen,[3] Klemm and Wahl,[4] Kuhn *et al.*[5] and Parker *et al.*[6] claimed that MgTe has the hexagonal WZ ground state structure. On the contrary, Yeh *et al.*,[7] Van Camp and Van Doren,[8] Chaudhuri *et al.*[9] Duman *et al.*[10]Duman and Li *et al.*[11] argued that the ground state of MgTe is with the NA structure. According to Phillips' ionicity (f_i) argument, the structure is four-fold coordinated if $f_i \leq 0.785$ and is six-fold coordinated if $f_i > 0.785$.[12] Since the ionicity of MgTe is 0.554, its ground state should be with four-fold coordinated WZ structure rather than with six-fold coordinated NA structure. At high pressure, the RS and the NA structures are two familiar candidates transformed from the WZ. Interestingly, the WZ→NA transition has only been found in the MgTe until now. The transitional pressure p_t is in $1 \sim 3.5$ GPa[11] reported in the high pressure energy-dispersive x-ray diffraction study and 1.1 GPa[13] predicted by first- principles calculations. Furthermore, at much higher pressure ($\sim$ 42.7 GPa), a second-order displacive phase transition from the NA (B8) to an orthorhombic MnP-type structure ($Pnma$, B31) driven by the softening TA_2(M) mode was demonstrated by Li *et al.*[14]

Recently, some researchers dedicated to elucidate the microscopic mechanism from four coordinated to six coordinated structure transition, for instance, WZ→RS,[15−19] WZ→NA,[13] ZB→RS,[20−24] and ZB→NA.[25,26] These studies have shed some light on the transitional course at atomic scale. Only understanding how one structure transforms into another structure, i.e. phase transition path or mechanism, could we catch the nature of high-pressure phase transition. The more profound meaning of the study on phase transition mechanisms is that it will promote the theoretical and experimental studies on how to control or manipulate the transition and accordingly synthesize new high-pressure phases. However there is not any report on how to utilize these transitional mechanisms to manipulate the transition. For the WZ→RS, an orthorhombic strain deformation path[15] or triaxial strain mechanism[17] has been presented. For the WZ→NA, the relative shifting of a density-packed Mg-atom layer in the $[\bar{1}010]$ or its equivalent directions with the $b/3$ relative displacement constraint is the transitional mechanism.[13] If we compare two transitional paths, a significant difference can be found. For the WZ→NA, three lattice parameters a, b and c of an orthorhombic cell (see Fig. 1(a)) decrease when volume collapse occurs. However, for the WZ→RS, one lattice parameter a lengthens and the others shorten. This difference provides us with a possibility to control the high pressure phase transition of the WZ structure. If the transition is irreversible, a new metastable phase might be synthesized. In addition, some compounds without any special control occur irreversible transitions under high pressure, such as Eu_2O_3[27] and metastable structures, can also be obtained.

In this Letter, the feasibility of manipulating phase transition is investigated by first-principles calculations within the framework of the density of functional

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theory (DFT) with the CASTEP code.[28] Ultrasoft pseudopotentials are expanded within a plane wave basis set with a cutoff energy of 380 eV. Pseudo atomic calculations are performed for Mg $2p^6 3s^2$ and for Te $5s^2 5p^4$. We use the generalized-gradient approximations (GGAs) in the scheme of Perdew–Burke–Ernzerhof (PBE)[29] to describe the exchange and correlation potential. The $\boldsymbol{k}$-point separations in each of the three reciprocal lattice directions are around 0.04 (1/Å). The structural optimizations without any constraint are considered to be converged when energy change, maximum stress, maximum force and maximum displacement are below 1×10^{-7} eV/atom, 1×10^{-4} GPa, 1×10^{-3} eV/Å and 1×10^{-5} Å, respectively. The above cutoff energy and convergence criterions are strictly examined to ensure to obtain the precise lattice constants and minimal enthalpy even in a very flat enthalpy hypersurface region. MgTe is chosen with two reasons. The first is such that p_t is relatively low. Therefore, the theoretical study is easy to be experimentally confirmed in the future. The second is such that both the WZ and the NA phases are found under ambient conditions. Thus the WZ→NA transition should be irreversible, which implies that the WZ→RS might be irreversible in view of the same neighbor environment for cation or anion in both the RS and the NA. Three structures of MgTe are shown in Fig. 1.

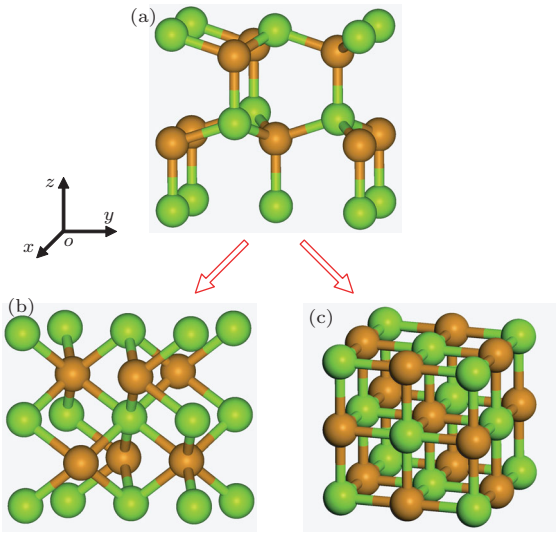


Fig. 1. (Color online) (a), (b) and (c) are wurtzite-type, NiAs-type and rocksalt-type MgTe cells, respectively.

As is well known, the equilibrium transitional pressure p_e at which the enthalpies of two structures are equal is generally determined by two equivalent methods. One is minimizing the total energy with respect to the structural parameters at constant volume. The common tangent of two total energy-volume curves will give the p_e values. The other is directly minimizing the enthalpy at a constant pressure. Then the two enthalpy-pressure curves will cross at p_e.[30] The latter is chosen in this study.

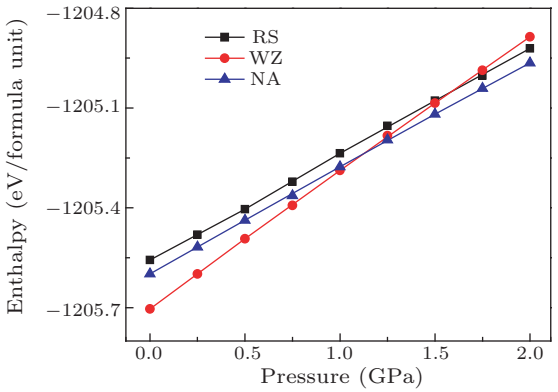


Fig. 2. (Color online) Enthalpy per formula unit as a function of pressure.

Figure 2 shows the enthalpies of the WZ-, NA- and RS-type MgTe as a function of pressure. It can be seen that the WZ structure will firstly transform into the NA structure and $p_e \sim 1.1$ GPa. Supposing that the WZ-type MgTe can transform into the RS rather than the NA structure, the corresponding p_e is about 1.6 GPa. The two enthalpy-pressure curves of the NA- and the RS-type MgTe are almost parallel and the distance between them is $\sim$ 0.04 eV per formula unit at a certain pressure. Thus the RS-type MgTe should exist neither under ambient conditions nor at hydrostatic pressure. To achieve the WZ→RS transition, we must prevent the WZ→NA happening. The distinctive changing features of lattice parameters in the WZ→NA and the WZ→RS have shed some light on how to control phase transition. For the WZ→NA at 1.1 GPa, the corresponding changes of a, b and c are 4.563 Å→ 4.159 Å (↓), 7.836 Å→7.210 Å (↓) and 7.302 Å→6.799 Å (↓). Similarly, the changes are 4.552 Å →5.861 Å (↑), 7.747 Å →5.861 Å (↓) and 7.306 Å →5.861 Å (↓) for the WZ→RS at 1.6 GPa. The arrow in parenthesis denotes the lattice parameter increasing or decreasing during the phase transitions. The essential difference in the two kinds of transition is that a increases for the WZ→RS and decreases for the WZ→NA. Thus making the cell free to expand in the a direction might impel the WZ to transform to the RS structure. Taking advantage of this feature, we firstly design a simple loading method, i.e. exerting equal biaxial pressure on the planes perpendicular to the b and c axes. More properly speaking, the pressure is loaded on the $(10\bar{1}0)$ and (0001) planes of a hexagonal cell or the (010) and (001) planes of an orthorhombic cell of the WZ-type MgTe. By monitoring the optimization trajectories, we find the symmetry of MgTe firstly changes from the WZ to a little distorted WZ and then suddenly to an orthorhombic structure with the pressure increasing. Meanwhile, the corresponding enthalpy firstly linear increases with pressure. Then there is an abrupt enthalpy change at ∼2.75 GPa as

shown in Fig. 3, which implies a phase transition happening. In particular, the fractional coordinates of the Te atoms in the orthorhombic cell change from original values to $(x, y, 0.5)$ or $(x, y, 1)$. With pressure continuously increasing to 5 GPa, the enthalpy-pressure curve is linear again. In the whole loading course, the MgTe structure is orthorhombic. While the pressure is unloaded, the enthalpy decreases linearly until it reaches zero without any abrupt change. At a pressure of less than 2.1 GPa, the enthalpy at unloading condition is more than that at loading mode. Therefore the MgTe is a metastable structure in the region of 0–2.1 GPa. Furthermore, the difference of enthalpy-pressure curves of loading and unloading conditions implicates that the transition is irreversible. With pressure decreasing, the orthorhombic structure relaxes its lattice parameters to minimize the total energy and finally transforms to a cubic RS structure with lattice parameters $a = b = c = 5.989$ Å at 0 GPa. Hence by means of a simple loading method, a metastable RS-type MgTe is obtained due to the irreversibility of phase transition. Figure 4 shows the volume change at loading and unloading pressure. Volume collapse occurs in the same pressure region as that of enthalpy abrupt change. The relative volume change at 2.75 GPa is 0.810. While pressure is unloaded, volume smoothly increases without abrupt change.

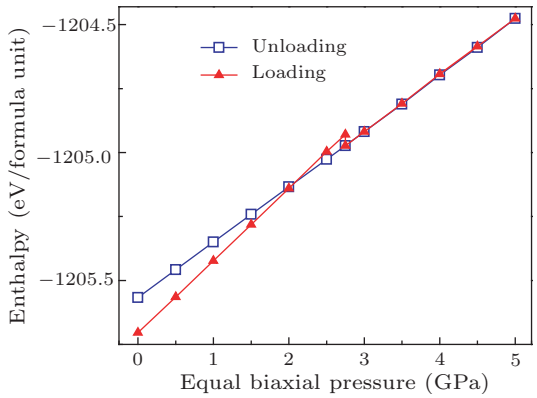


Fig. 3. (Color online) Enthalpy per formula unit as a function of equal biaxial pressure.

Besides the structural optimizations at equal biaxial pressure, we have investigated the effect of unequal biaxial pressure on the cell in Fig. 1(a). The pressure region investigated (0–5 GPa) can be divided into two parts as shown in Fig. 5. Region I is an untransitional region in which the structure keeps to hexagonal symmetry with a tiny distortion. No volume collapse occurs. Region Ⅱ is a transitional region in which the WZ transforms to an orthorhombic structure with unequal lattice parameters ($a \neq b \neq c$). There is a volume abrupt change. Similar to equal biaxial pressure, while the pressure is decreased to zero the a, b and c of the orthorhombic structure become equal and the RS structure is left.

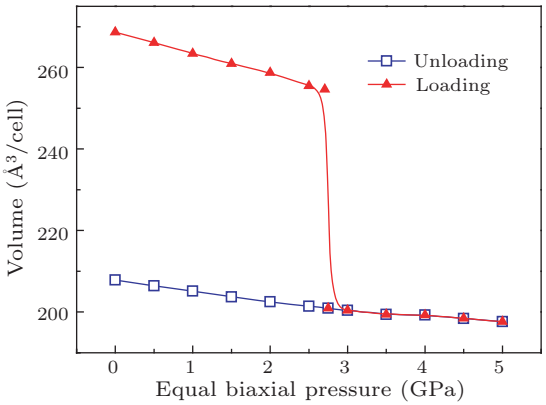


Fig. 4. (Color online) Volume per cell as a function of pressure.

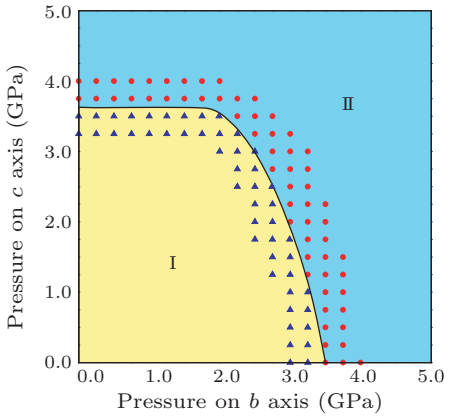


Fig. 5. (Color online) Untransitional region (I) and transitional region (Ⅱ) under biaxial pressure.

In conclusion, the controllability of phase transition is investigated by the first-principles density functional theory. Based on the WZ→NA and the WZ→RS transition mechanisms, we predict that a new metastable RS-type high-pressure phase of MgTe can be synthesized by loading biaxial pressure on $(01\bar{1}0)$ and (0001) planes of the hexagonal WZ cell. Due to the irreversibility of the WZ→RS, the RS-type MgTe is left until it reaches an ambient condition. This study might be helpful for synthesizing a new high-pressure phase by controlling phase transition. We expect that this theoretical study can be confirmed in the future according to the final transition product resulting from high-pressure experiments.

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