I4/mmm Phase of MgF$_2$: An Ab Initio Molecular Dynamics Study[1]

Hülya Öztürk, Cemile Kürkçü, and Cihan Kürkçü

Fizik Bölümü, Ahi Evran Üniversitesi, Kırşehir 40100, Turkey
e-mail: hozturk@ahievran.edu.tr; hulyaozturk@gazi.edu.tr

Abstract—A constant pressure ab initio technique is applied in order to study the structural response of magnesium fluoride (MgF$_2$) under the hydrostatic pressure up to 800 GPa. The orthorhombic-to-tetragonal phase transformation of MgF$_2$ is obtained at 720 GPa. This phase transition is also analyzed from the total energy and enthalpy calculations, and it is found that this phase change should occur around 260 GPa. As far as we know, this tetragonal phase has not been obtained in any previous studies.

INTRODUCTION

The investigation of materials under high pressure has become a very important topic in recent years. The high-pressure behavior of MgF$_2$ is reasonably inquisitive. Inquisitive structural features of phase transformation mechanism are still mysterious because of difficulties in monitoring movements of atoms in the experiments. Reliable dynamical simulations are needed because of the difficulties in understanding the atomistic motions while performing the experiments.

Whereas some studies [1–4] give prominence to that the tetragonal rutile-type MgF$_2$ should be transformed into an orthorhombic CaCl$_2$-type structure with space group *Pnnm*, some other studies [5–11] underline that this material should be transformed into a cubic fluorite-type structure with space group *Fm$\bar{3}$m* at high pressures. The results of our recent study [11] support the later transformation.

MgF$_2$ crystallizes in a tetragonal rutile-type structure with space group *P4$_2$/mnm* at ambient conditions. Although this crystal also has the same rutile-type structure as the transition metal compounds of AF$_2$-type, Mg is not a transition metal; namely, Mg has no *d*-electrons. Lack of these electrons and the highly ionic character of MgF$_2$ simplify theoretical studies. The phase transitions of MgF$_2$ are found at lower pressures than in many dioxides due to the higher compressibility of this material and relative sizes of its ions. The goal of this study is to investigate the possibility of existence of still unknown stable or intermediate MgF$_2$ phases.

COMPUTATIONAL DETAILS

The computations were achieved using the ab-initio program SIESTA based on pseudopotentials and a localized basis set [12]. Calculations were performed in the density functional theory (DFT). For the exchange-correlation energy the generalized gradient approximation (GGA) was performed [13]. Double zeta plus polarized basis sets were applied. A uniform mesh with a plane wave cut-off of 150 Rydberg was used with the purpose of representation of the electron density, the local part of the pseudopotentials, the Hartree and the exchange-correlation potential. A simulation cell of 96 atoms was selected and the periodic boundary conditions were used. Gamma point sampling was employed for the Brillouin zone integration.

To apply pressure to the system, conjugate-gradient method was used. Firstly the system was relaxed at zero pressure, after that pressure was increased step by step. For each value of the applied pressure, the structures were allowed to relax and to catch their equilibrium volumes and lowest energies by optimizing their lattice vectors and atomic positions together until the maximum atomic forces were getting smaller than 0.01 eV Å^{-1} and the stress tolerances were getting less than 0.5 GPa.

RESULTS AND DISCUSSIONS

We can principally determine relative stability of different phases of materials under finite pressure and temperature by a simple compression of their Gibbs free energies given by

$$G = E_{\text{tot}} + PV - TS. \qquad (1)$$

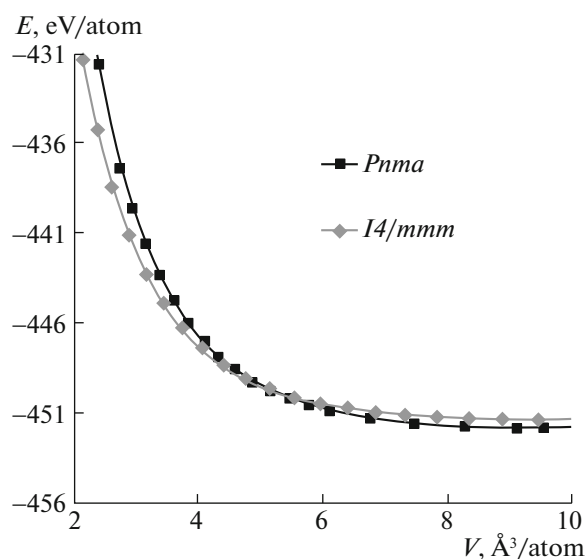[1] The article is published in the original.

Fig. 1. Total energies of the orthorhombic structure with space group *Pnma* and the tetragonal structure with space group *I4/mmm* as a function of volume.
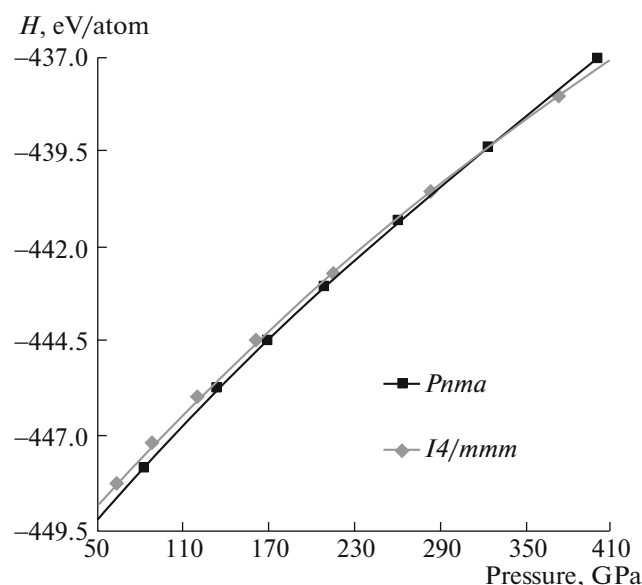

Fig. 2. The enthalpies of the orthorhombic structure with space group *Pnma* and the tetragonal structure with space group *I4/mmm* as a function of pressure.

Since calculations are made at zero temperature, the TS term is neglected. Therefore, the static enthalpy can be expressed as

$$H = E_{tot} + PV, \qquad (2)$$

where pressure is obtained by direct differentiation of the calculated energy-volume curves i.e.,

$$P = -dE_{tot}/dV. \qquad (3)$$

For the reason that the two phases have the same enthalpy at the phase transition, the transition pressure can be easily found by equating the enthalpy of the two phases.

We take the energy-volume calculations into account and the thermodynamic criterion of equal free energies to study the stability of different phases of MgF_2. The calculated energy–volume relations are fitted to the third-order Birch−Murnaghan equation of states given by

$$P = 1.5B_0\left[(V/V_0)^{-\frac{7}{3}} - (V/V_0)^{-\frac{5}{3}}\right]$$
$$\times \left\{1 + 0.75(B_0' - 4)\left[(V/V_0)^{-\frac{2}{3}} - 1\right]\right\}, \qquad (4)$$

where P is the applied pressure, V is the volume at pressure, V_0, B_0, and B_0' are the volume, bulk modulus and its pressure derivative at ambient pressure [14, 15]. While dimensional forms of P and B_0 are $ML^{-1}T^{-2}$, V and V_0 are L^3, B_0' is dimensionless. Figure 1 shows the computed total energies of the orthorhombic structure

with space group *Pnma* and the tetragonal structure with space group *I4/mmm* as a function of volume.

For the reason that structural phase transitions in simulations occur through the entire simulation cells, systems need to cross a notable energy barrier for transition from one phase to another phase. Enthalpy calculations give commonly realistic transition pressures relative to experimental transition pressures. The phase transitions emerge when the enthalpies of the two phases equal to each other. Thus, we compute the enthalpies of the phases and plot them as a function of pressure in Fig. 2.
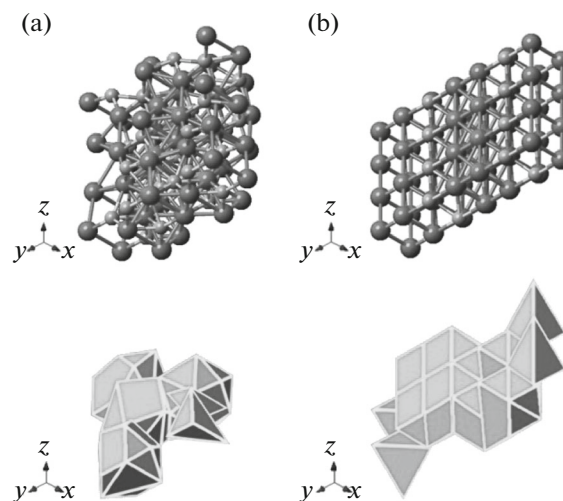

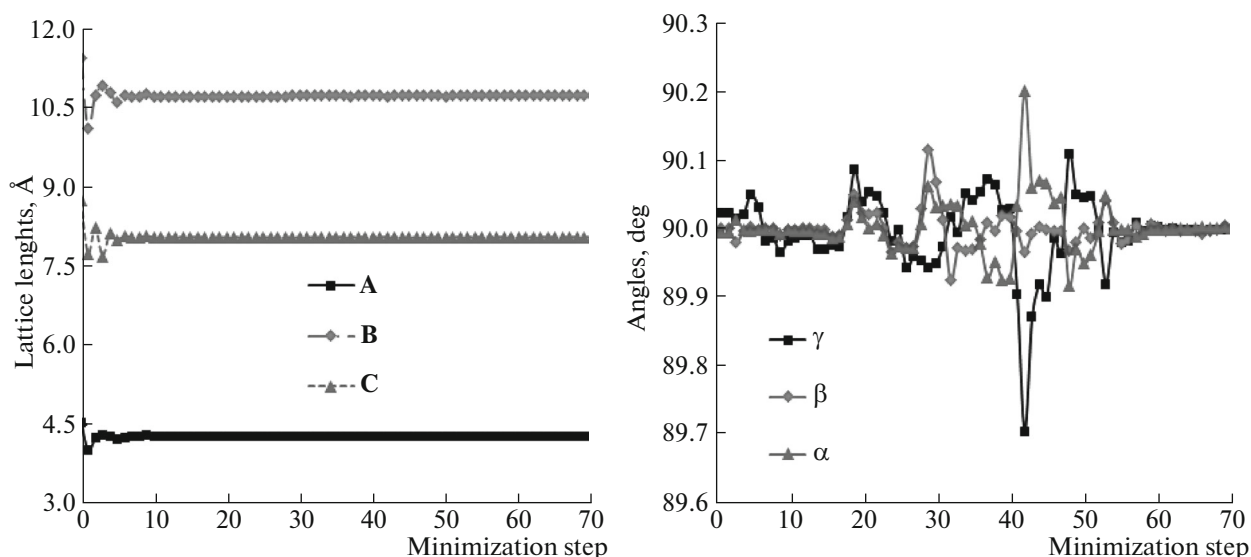**Fig. 3.** Crystal structures of MgF_2: at (a) 500 and (b) 720 GPa.

Fig. 4. Variation of the simulation cell lengths and angles as a function of minimization step at 720 GPa.

We can conclude from enthalpy curves that the phase transformation from the orthorhombic structure with space group *Pnma* to the tetragonal structure with space group *I4/mmm* occurs at about 260 GPa. These structures with polyhedral views are depicted in Fig. 3.

Although literature data comparison of the orthorhombic structure with space group *Pnma* is given in our previous study [11], the tetragonal structure with space group *I4/mmm* is obtained for the first time in this study. Therefore, numerically obtained results of this tetragonal structure have not compared with the literature.

In order to clarify the mechanism of this phase transition, the simulation cell vectors and angles should be tested. These cell vectors expressed as **A**, **B**, and **C** correspond to the [100], [010], and [001] directions in the beginning. Figure 4 illustrates variation of the simulation cell lengths and angles as a function of minimization step at 720 GPa.

In order to explore whether there is any intermediate state during the phase transformation or not, we investigated the structure found in that study at each minimization step using the KPLOT [16] program. Although we analyzed this structure at each minimization step using this program, we did not find any intermediary phase.

CONCLUSIONS

We have used a constant pressure ab initio technique to study the behavior of MgF₂ under the hydrostatic pressure. The effect of temperature on the pressure of phase transition is neglected since calculations are made at zero temperature. The orthorhombic structure with space group *Pnma* of MgF₂ transforms to tetragonal structure with space group *I4/mmm* at 260 GPa. The Mg−F bond lengths range from 1.839 to 1.999 Å and Mg is ten-fold coordinated by F and the F−F bond lengths range from 1.828 to 2.274 Å and F is five-fold coordinated by Mg for this tetragonal structure. As far as we know, this tetragonal phase obtained in this study has not been observed in any other earlier studies.

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