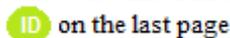




Phase transition of GeO₂ crystal at high pressure: An ab initio molecular dynamics study

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ABSTRACT

The phase transition of GeO₂ structure was studied under constant pressure by using ab initio calculation and the generalized gradient approximation (GGA). A structural phase transition was observed at 30 GPa for the first time under the constant hydrostatic pressure, and P4₂/mnm structure was transformed into a CaCl₂ (Pnmm) structure. This phase transition was also investigated using total energy, enthalpy, and the phase shift calculations. It was determined that the obtained transformation parameters and bulk modulus properties were compatible with the previous experimental and theoretical first principle calculations.

Keywords: High pressure, molecular dynamic, enthalpy.

GeO₂ kristalinin yüksek basınçta faz geçişi: Bir ab initio moleküler dinamik çalışması

ÖZ

GeO₂ yapısının faz geçişi, sabit basınçta ab initio hesaplaması ve genelleştirilmiş gradyan yaklaşımı (GGA) kullanılarak incelenmiştir. Yapısal faz dönüşümü sabit hidrostatik basınç altında ilk kez 30 GPa'da gözlemlendi ve P4₂/mnm yapısı CaCl₂ (Pnmm) yapısına dönüştü. Bu faz geçişi, toplam enerji, entalpi ve faz kayması hesaplamaları kullanılarak da araştırılmıştır. Elde edilen dönüşüm parametrelerinin ve yığın modül özelliklerinin, önceki deneysel ve teorik birinci prensip hesaplamalarıyla uyumlu olduğu belirlenmiştir.

Anahtar Kelimeler: Yüksek basınç, moleküler dinamik, entalpi.

1. INTRODUCTION

It is important to understand atomic structures of nano-dimensional materials, and behavior of the material under high pressure in material science and application of geological, physical and chemical materials. Empirical research in the literature has played an important role in understanding the phase change caused by the pressures of many materials. However, it has been difficult to interpret the experimental results of some materials over the last two decades. The structural and electronic structure of GeO₂ in tetragonal rutil type structure with space group P4₂/mnm have been studied in the past extensively.¹⁻⁵ The structural, electronic and optical properties of GeO₂ under high pressure and temperature have been investigated using different experimental techniques and theoretical calculations.¹⁻⁷ Under ambient conditions, GeO₂ which is a crystalline compound has two crystalline forms: α-GeO₂ quartz-

type phase P3₂21⁸ and r-GeO₂ P4₂/mnm phase with rutil structure.⁹ In the r-GeO₂ rutil phase, GeO₄ is characterized by a tetrahedral structure with four oxygen atoms surrounding a germanium atom. The α-GeO₂ phase is characterized by a GeO₆ octahedral structure containing six oxygen atoms surrounding a germanium atom. The crystalline sample also has showed complex behavior at high pressures and temperatures where several additional structural transformations have been observed.¹⁰ In addition, molecular-dynamic calculations have been made to investigate the behavior of GeO₂ under high pressure. Lodziana and co-workers have performed ab initio calculations of GeO₂ and observed phase transition from rutil-type structure to CaCl₂-type structure at around 19 GPa.² Using angle-dispersive X-ray powder-diffraction data, a transition has been observed from rutil to CaCl₂ type GeO₂ structure at 36 GPa.³ Second-order phase

transition from rutile-type to CaCl_2 -type has also been observed in GeO_2 at 26.7 GPa by raman spectroscopy.⁵ High pressure studies have been performed using extended X-ray absorption fine structure (EXAFS) spectroscopy,^{6,7,11} X-ray diffraction and neutron diffraction experiments.¹²⁻¹⁴ All experimental studies agree that the number of coordination between Ge-O changes at a pressure range of 3-15 GPa. EXAFS studies have shown that the bond length of Ge-O ranges from 1.74 (0 GPa) to 1.8 (13 GPa).¹¹ In the first study to address this issue, Itie and co-workers have measured X-ray radiation absorption up to 23.2 GPa and found that the Ge coordination has passed from four-fold to six-fold under the pressure of 7 to 9 GPa.⁷ Vaccari has not found evidence of a six-fold structure despite the high pressures being raised to around 13 GPa.¹¹ The latest X-ray absorption fine structure (XAFS) and EXAFS studies^{6,15} have also been extended to 53 and 44 GPa, respectively, in the working interval, and it has been estimated that only 25-30 GPa was reached for six-fold coordination of Ge ions. The application of high pressure is a powerful tool for examining the structural and electronic properties of crystal materials.

Here, a new contribution of this article is to examine the change in the physical Phase transition properties of the GeO_2 crystal under high pressure with an ab initio molecular dynamic study. This study is an original study since it has not been studied in the literature before.

2. METHOD

The Parrinello-Rahman method has been used to investigate phase-based transitions in various materials, mostly to investigate crystal-to-crystal phase transitions in small-sized cells. In these simulations; the transformation mechanism, the formation and the structural and electronic properties of the phases under pressure can be easily explained. In this study, hydrostatic pressure was applied to the simulation cell, and calculations were made using SIESTA code¹⁶ and the program density functional theory (DFT) based on the ab initio (first-principle) pseudopotential method. For Khon Sham Hamiltonian, Troullier-Martin was chosen as the "norm-conserving pseudopotential" along with the GGA using the exchange-correlation function of Ernzerhof and Perdew-Burke.^{17,18} The double-zeta plus polarization numerical base set was selected with a kinetic energy cut-off of 600 meV. The simulation cell in which periodic boundary conditions are used consists of 96 atoms. We used a regular mesh with the plane-wave cut-off of 150 Ry to express the numerical base set and the electron density, the local part of the pseudopotentials, the Hartree and the exchange

correlation potential, and the Γ point shape for the 96 atomic simulation cell. It is used for Broullin region integration and because of the energy difference of 0.03 eV/atom between the 96 atomic simulation cell and the 256-k point, 2 atomic primitive cell. The reason for choosing this community is to remove the thermal surge so that the structure is more easily inspected during the phase transition. Pressure was applied via the Parrinello-Rahman method.¹⁹ The system is initially balanced at zero pressure and then the pressure is gradually increased by increments of 10 GPa. The balancing period consists of 1000 steps with each step being 1 fs. In addition, 'Power Extinguishing Technique' has been used throughout MD simulations. Energy volume calculations were carried out in unit cells of rutile and CaCl_2 . The Brillouin region integration was calculated with $8 \times 8 \times 8$ and $10 \times 10 \times 10$ k-point squares automatically generated by Monkhorst and Pack approach for rutile and CaCl_2 phases respectively.²⁰ We have used the KPLLOT program that provides detailed information about the cell parameters, the space group and the atomic position of a given structure.²¹ The tolerances of 0.2 Å, 4° and 0.7 Å are used for bond lengths, bond angles, interplanar spacing.

3. RESULTS AND DISCUSSION

Pressure-volume graph in Figure 1 was drawn to classify the phase transition of GeO_2 by pressure effect in the thermodynamic category. As seen from this graph, the volume of GeO_2 varies suddenly when the simulation pressure is increased from 20 to 30 GPa. The pressure-volume curve shows a discontinuity at this point.

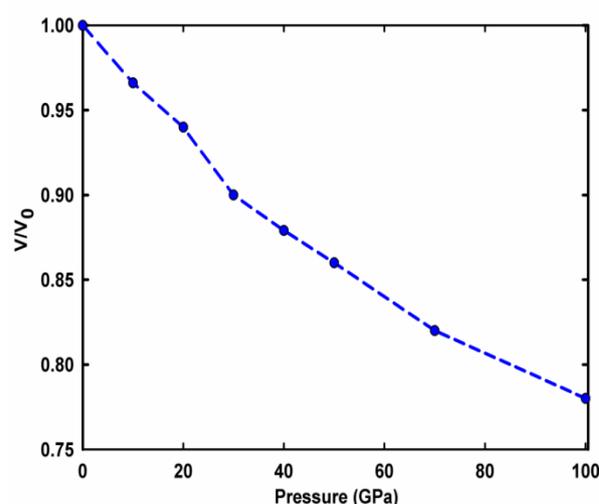


Figure 1. The volume-pressure plot (y axis shows normalized values).

Because the Gibbs free energy is equal to the derivative volume in relation to the pressure at constant temperature, the pressure-based phase transition unit exhibits a sudden change from one phase to another in the volume of the cell. Since there is a second degree phase transition, there is no sharp decrease on the volume- pressure plot in Figure 1, we can observe the sharp decrease in the first degree phase transition. The symmetry change in the phase transition was determined by the group theory method. The structure obtained for each pressure value applied in the simulation program was analyzed symmetrically using the KPLOT program.²¹

At 30 GPa simulation pressure, it was observed that the crystal lattice structure passes from the rutile structure ($P4_2/mnm$) to the $CaCl_2$ structure ($Pnmm$), and it is shown in Figure 2a-d. The structural parameters and atomic positions of the initial structure and the structure at 30 GPa are given in Table 1. In a detailed analysis of 30 GPa, the rutile symmetry continued to 969 time step and in step 970 it was converted to the $CaCl_2$ structure. We obtained the lattice constants as $a = 4.420 \text{ \AA}$, $b = 4.420 \text{ \AA}$ and $c = 2.914 \text{ \AA}$ for rutile structure ($P4_2/mnm$) and $a = 4.374 \text{ \AA}$, $b = 4.134 \text{ \AA}$ and $c = 2.844 \text{ \AA}$ for $CaCl_2$ structure ($Pnmm$). This result is a definite proof that GeO_2 returns to the $CaCl_2$ structure under high pressure.

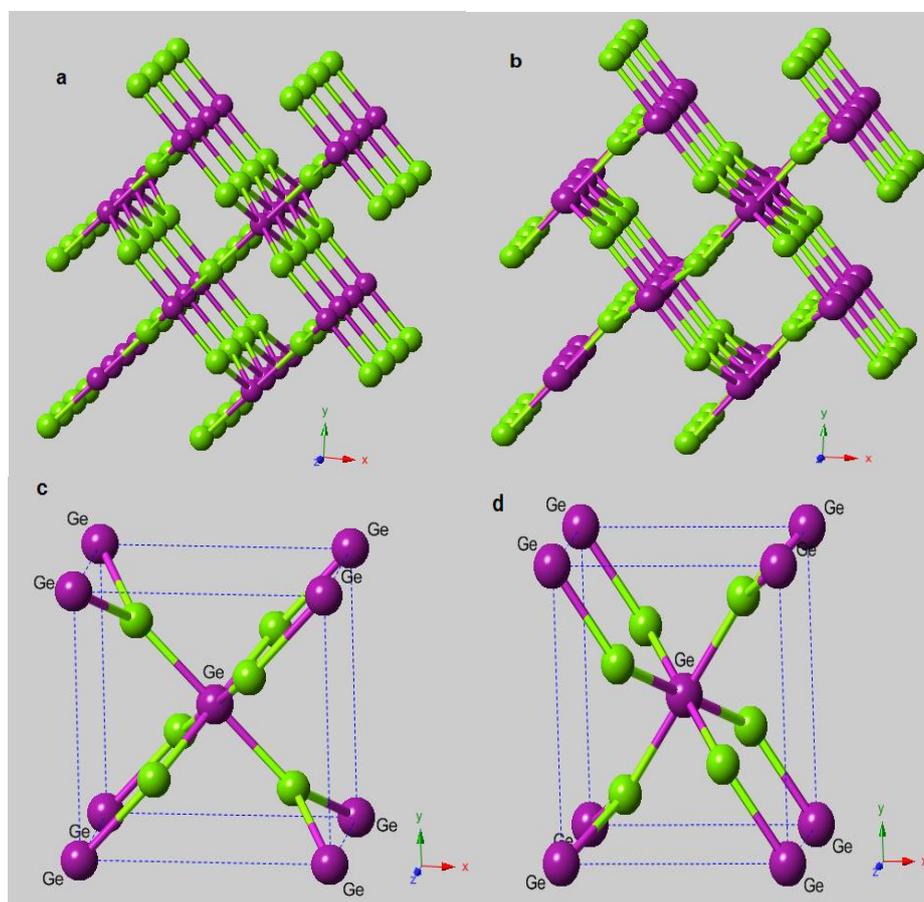


Figure 2. Crystal structures of GeO_2 $P4_2/mnm$ at zero pressure and $Pnmm$ at 30 GPa (a: $P4_2/mnm$ simulation-cell, b: $Pnmm$ simulation-cell, c: $P4_2/mnm$ unit-cell and d: $Pnmm$ unit-cell, respectively).

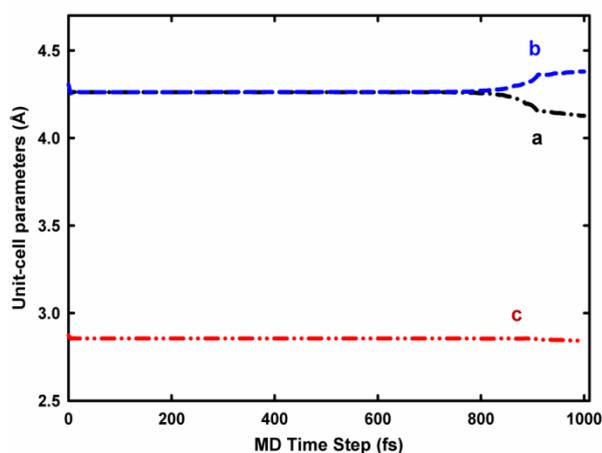
Table 1. The fractional coordinates and lattice parameters of GeO₂ at 0 and 30 GPa.

Structure	a (Å)	b (Å)	c (Å)	x	y	z	Angles
Rutile	4.420	4.420	2.914	Ge:0.000	0.000	0.000	90, 90, 90
				O: 0.306	0.306	0.000	
CaCl ₂	4.375	4.134	2.844	Ge:0.000	0.000	0.000	90, 90, 90
				O: 0.2745	0.6687	0.000	

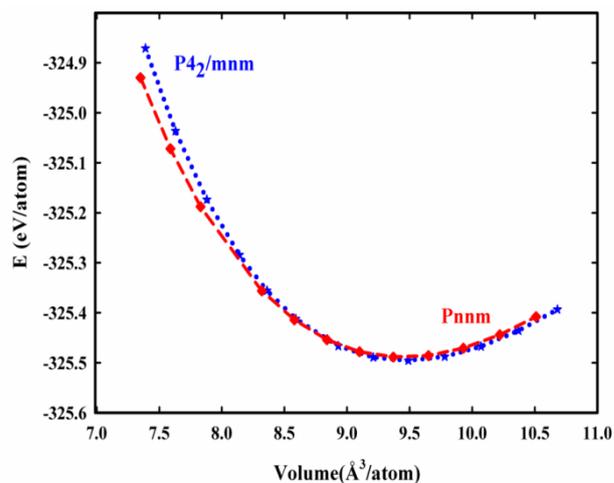
Table 2. Lattice parameters (a, b, c), B₀, c/a and u for P4₂/mnm and Pnmm phases of GeO₂

Structure	a (Å)	b (Å)	c (Å)	B ₀ (GPa)	c/a	u	Ref.
Rutile	4.420	4.420	2.914	269	0.643	0.306	This study
	4.407	4.407	2.862		0.649	0.306	(1)
	4.384	4.384	2.864	250	0.653	0.306	(2)
	4.397	4.397	2.863		(3)		
	4.492	4.492	2.923		0.660	(4)	
CaCl ₂	4.375	4.134	2.844	259			This study
	4.258	4.203	2.805				
	4.281	4.143	2.798	(2)			
	4.263	4.263	2.815	262			(3)
	4.364	4.422	2.854	(4)			

As can be clearly seen in Figure 3, the system has undergone specific rearrangement after the 970th

**Figure 3.** The time evolution of the unit-cell parameters at 30 GPa.

simulation step. Separate volume–energy calculations for the rutile and CaCl₂ phases of GeO₂ were performed.

**Figure 4.** The energy-volume plot as a function of the volume of the unit atom for GeO₂.

The graph of the data obtained from the total energy calculations is shown in Figure 4. The volume-energy curves obtained for each phase were fitted to the Birch-Murnaghan state equation. The cell parameters calculated for the high pressure phase together with B_0 values are given in Table 2. Finally, enthalpy calculations were performed to determine exactly at which pressure GeO_2 passed from the rutile crystal structure to the CaCl_2 crystal structure. Structural phase transformations in simulations occur in all simulation cells. Systems must pass an important energy barrier to transform from one phase to another. This means that simulated structures must be under extreme pressure to achieve a phase transition. In addition, the absence of thermal movement in our simulations shifts the transitions to a higher pressure. On the other hand, free energy $G = E_{\text{tot}} + PV - TS$ should be used to determine the most stable structure at finite pressure and temperature. Density functional calculations are made at zero kelvin temperature and entropic additives can be neglected. Therefore, enthalpy values, including pressure-volume effects, $H = E + pV$ were calculated.

The enthalpy for both the rutile phase and the CaCl_2 phase of GeO_2 can be calculated using the calculated volume-energy data for each phase. As shown in Figure 5, the enthalpy of the crystal structure of the rutile formed by the stable atomic order of GeO_2 up to a certain pressure value is increased by the increase of the pressure. After a certain pressure value, there is a structure with a free energy atomic array (CaCl_2) that is smaller than the free energy of the system. At this pressure value, the atomic sequence of the rutile phase material is unstable relative to the new atomic sequence. The phase transition caused by the pressure can be obtained from the cross-over of enthalpy-pressure curves (Figure 5).

The 36.5 GPa value calculated for the phase transition from Rutile to CaCl_2 is compatible with the 36 GPa experimental value.³ The values of the lattice parameters, bulk modulus, u value and c/a of GeO_2 in this study and in other theoretical and experimental studies are summarized in Table 2. The lattice parameters calculated for the phase of GeO_2 in ambient conditions and the phase at high pressure are in agreement with the bulk modulus of the theoretical and experimental studies. The rutile- CaCl_2 transition pressure has a new phase-transition pressure value which is different from the theoretical and experimental transition pressure values previously found. The electronic density of state (EDOS), the electronic property of GeO_2 , is calculated for pressures of 0 and 30 GPa and is given in Figure 6. From this figure, it is seen that GGA band gap are found as 1.15 eV at zero pressure and 2.62 eV at 30 GPa. Despite increasing band gap energy, it shows semiconductor property. In Figure 7, the values of a , b and c of the simulation

lattice parameters are given as a function of applied pressure. It was seen that there was a decrease in a , an increase in b , and no change of c at 30 GPa.

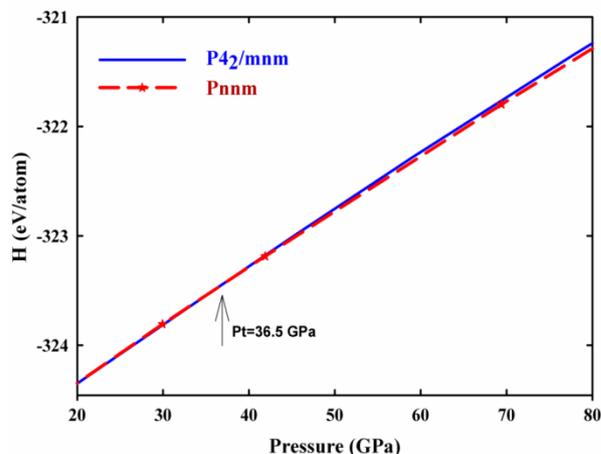


Figure 5. The enthalpy curves of $P4_2/mnm$ and $Pnnm$ phases of GeO_2 .

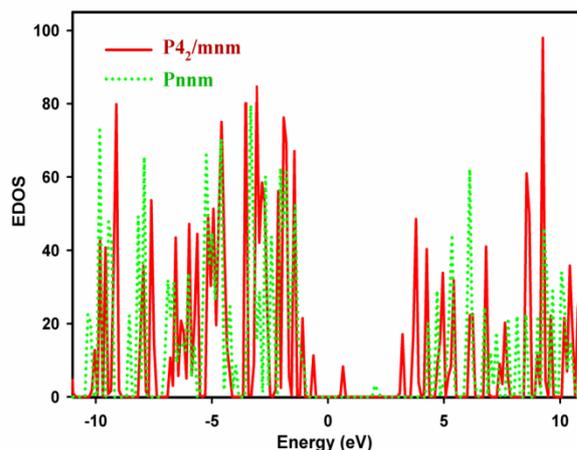


Figure 6. The electronic density of states (EDOS) for GeO_2 phases.

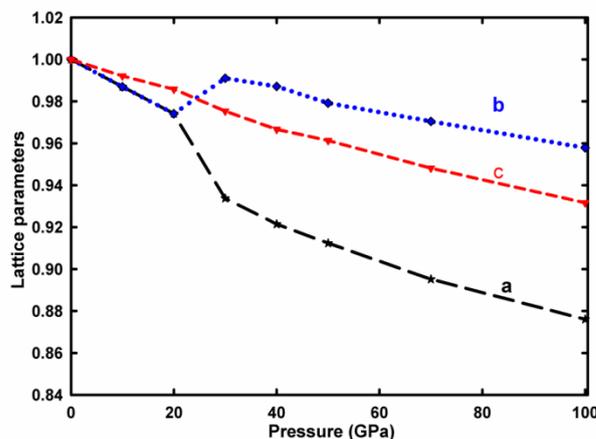


Figure 7. The lattice parameters-pressure plots for GeO_2 .

Using a constant pressure ab initio technique, GeO₂ has been studied on rutile-CaCl₂ phase transition and similar phase transitions for CrO₂ have been observed in previous study by Alptekin.²² Similarly, ab initio molecular dynamic studies have been performed on ZrO₂²³ and MgF₂ constructs.²⁴ In an experimental study, transitions from rutile to CaCl₂ phase have been observed by Prakapenka and co-workers¹ and in this experimental study lattice constants for rutile were found as a=4.407 Å, c=2.862 Å and lattice constants for CaCl₂ have been found as a = 4.258 Å, b = 4.203 Å and c = 2.805 Å. At the same time, the c/a = 0.649 and u = 0.306 have been estimated by, Prakapenka and co-workers.¹ The values we obtained are c / a = 0.643 and u = 0.306 and are compatible with the results in the literature. In another experimental study, rutile lattice constants have been found as a = 4,397 Å, c = 2,863 Å and lattice constants for CaCl₂ have been found as a = 4,263 Å, b = 4.263 Å, c = 2.815 Å by Haines and co-workers.³ and similarly, bulk modulus B₀ = 250 GPa and B₀ = 262 GPa.

In this study, we found these values for the rutile phase as a = 4.420 Å, c = 2.914 Å and B₀ = 269 GPa; and for CaCl₂ phase as a = 4.375 Å and B₀ = 259 GPa. In Table 2, our results were compared with other studies. In similar studies, wurtzite (WZ) and zinc-blend were studied using the constant pressure MD technique for CdSe and BeO.²⁵⁻²⁷

4. CONCLUSIONS

In this study, the rutile and CaCl₂ structure change of GeO₂ under high pressure was investigated. The phase transition was observed to pass from the tetragonal rutile structure to the orthorhombic CaCl₂ structure. The pressure was applied between 0 and 100 GPa with ab initio constant pressure technique and a phase transition was first observed at 30 GPa. Furthermore, the total energy and enthalpy calculations were based on the enthalpy-pressure graph of phase transition around 36.5 GPa. In theoretical and experimental studies on the GeO₂, crystal phase transitions were observed at 19 and 36 GPa. The electronic density of state (EDOS) for high pressure phases were calculated for GeO₂ and electronic calculations indicated that GeO₂ was still a semiconductor at 30 GPa. We obtained the the lattice parameters, bulk modulus and phase transition pressures which were in agreement with experimental and theoretical studies.

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Conflict of interests

Author declares that there is no a conflict of interest with any person, institute, company, etc.

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