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บทความวิจัย

การเปลี่ยนแปลงโครงสร้างในเทอร์นารี่แบบชนิดเวอร์ไซด์ไปยังร็อกซอลต์ของ $LiGaO_2$ จากการคำนวณแบบแอบอินิโช

Phase Transformations in Ternary Wurtzite-to-Rocksalt type of $LiGaO_2$ from Ab Initio Calculation

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บทคัดย่อ

การเปลี่ยนแปลงโครงสร้างของเทอร์นารี่เวอร์ไซด์ไปยังร็อกซอลต์ตามเส้นทางของ B4-B1 ใน LiGaO2 (LGO) ถูกศึกษาโดยใช้การคำนวณแบบแอบอินิโช ซึ่งจากผลการศึกษาพบว่าภายใต้สภาวะความดันรอบทิศทางที่ 3.7 GPa LGO จะแสดงพฤติกรรมเป็นโครงสร้างรูปแบบที่คล้ายร็อกซอลต์ซึ่งคือโครงสร้างแบบลูกบาศก์แบบกลางตัว (กรุปปริภูมิแบบ $I4_1$/amd) จากการคำนวณที่มากกว่านั้น ความเสถียรภาพของกระบวนการเปลี่ยนแปลงโครงสร้าง จะสามารถถูกแสดงออกมาได้โดยการคำนวณพื้นผิวเอนทัลปี ที่สามารถแสดงให้เห็นถึงพลังงานกีดกันของเส้นทาง ในการเปลี่ยนแปลงโครงสร้าง และท้ายที่สุดพลังงานกีดกันไปยังโครงสร้าง $I4_1$/amd สามารถคำนวณได้เท่ากับ 86.25 meV/atoms ยิ่งไปกว่านั้นพลังงานของการกีดกันในแนวขนานยังมีค่าต่ำกว่าในแนวตรงอีกด้วย

คำสำคัญ : การเปลี่ยนแปลงโครงสร้าง, LiGaO2, เส้นทาง B4-B1, แอบอินิโช

Abstract

A ternary wurtzite-to-rocksalt phase transformation, so called B4-B1 pathway, in $LiGaO_2$ (LGO) is investigated using ab initio calculation. The result reveals that under hydrostatic compression up to 3.7 GPa, LGO finally exhibits structure of a rocksalt-like with body-centered tetragonal (space group $I4_1$/amd) structure. According to further calculations, the stability of the phase transformation processes can be characterized by calculating surface enthalpy, which can be revealed energy barriers of the transformation paths. Finally, the energy barrier is discovered corresponding to the ($I4_1$/amd) structure at 86.25 meV/atoms. Furthermore, the energy barrier in parallel (in-plane) is lower than the straight diagonal path.

Keywords *:* phase transformations, $LiGaO_2$, B4-B1 pathway, ab initio

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Introduction

The wurtzite structure (B4) to rocksalt structure (B1) in binary semiconductors are practically significant for basic solid-state science and applied materials research. The B4-B1 phase transformations are an important transition pathway in A^NB^{8-N} binary semiconductors because of its widely used application of A^NB^{8-N} binary semiconductors. Many materials have been studied for the last few decades (Yan *et.al.*,2016; Limpijumnong & Jungthawan, 2004). A^NB^{8-N} binary semiconductor is a common crystalline form of wurtzite structure, such as ZnO, MgO and GaN. However, investigation of the pressure-induced structural transitions in I-II-VI_2 ternary wurtzite is also very important in both the theoretical and experimental aspects. One of the most interesting I-II-VI_2 ternary wurtzite materials is $LiGaO_2$ (LGO), which is one of the most suitable substrate for optoelectronic semiconductors for ZnO and GaN fabrication (Kang *et.al.*,1999;Chou *et.al.*,2011;Ying *et.al.*,2015;Zheng *et.al.*,2017). The LGO crystal structure at ambient phase is orthorhombic structure with space group $Pna2_1$, which is obtained from substitution group-II element, Zn, by group-III element, Ga, and group-I element, Li, respectively. Due to the relaxation of the oxygen sub-lattice, the LGO ternary oxide exhibits different structure from the wurtzite-type structure as in ZnO binary oxide (Limpijumnong *et.al.*,1996;Kamijoh & Kuriyama *et.al.*,1981) However, the understanding of pressure-induced structural transition of ternary wurtzite LGO following B4-B1 phase transformation in binary compound is unclear, especially the details of enthalpy surface between pathway of transition and enthalpy barrier.

In this work, Density Functional Theory (DFT) calculations have been used to investigate a homogeneous ternary wurtzite-to-rocksalt phase transformation of LGO. The result reveals a pathway following B4-B1 phase transformation of binary compound which initiate from the terinary-wurtzite-type of LGO ($Pna2_1$) to high-pressure rocksalt phases of LGO ($I4_1/amd$) by calculating enthalpy surface diagrams. Furthermore, the enthalpy barrier of the transformation is also considered.

Methods

The calculations in this work established based on the Density functional theory (DFT), performed using the Vienna *Ab* initio Simulation Package (VASP) (Kresse & Furthmuller *et.al.*,1996) with generalized gradient approximation (GGA). The projector augmented wave method (PAW) have been set up for DFT calculations (Perdew *et.al.*,1997). A unit cell of a LGO consists of 16 atoms (4 Li atoms, 4 Ga atoms, and 8 O atoms) has been setup (Figure 1). The calculation was performed on a 7×7×7 k-point (Monkhorst & Pack, 1976) mesh with plane wave expansions set up to 520 eV. The calculation was considered to be converged, when the force and the energy steps in the self-consistent field (SCF) cycles dropped below 0.1 meV/ Å and 0.1 meV/atom, respectively.

To identify stable crystalline structure under hydrostatic pressure, enthalpy of the system was analyzed as a function of lattice parameter ratios *c/a* and *b/a* (Limpijumnong & Jungthawan, 2004). For hydrostatic compression, the enthalpy (*H*) can be calculated as

$$H = E + pV, \qquad (1)$$

where *E* is the total energy per unit cell, *p* is the pressure, and *V* = *abc* is the volume of the unit cell. For each *c/a* and *b/a* pairs, the parameters and the volume *V* are allowed to relax until the structure that exhibit minimum *H* is obtained. After that, *c/a* and *b/a* has been individually decreased from 0.787 to 0.468 and 0.848 to 0.468, respectively with an interval of 0.05. Finally, the investigation will be applied on total 36 configurations of *c/a* and *b/a*. At each configuration, the minima of enthalpy will be calculated and recorded. Then, all enthalpy value has been plotting to create the enthalpy surface to investigate the behavior of phase transformation.

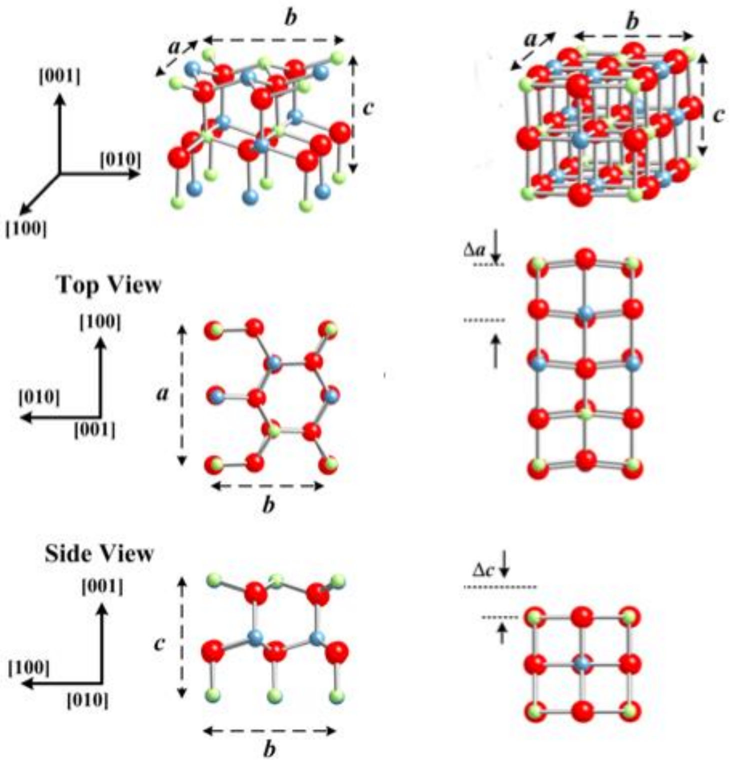

Figure 1 Schematic illustration of the orthorhombic (Pna2_1) structure at left column and Body-centered tetragonal (I4_1/amd) structure at right column of LGO: The middle row and the bottom row show the side view and top view, respectively. The crystal parameters *a* and *c* are indicated. Δ*a* and Δ*c* are the percentage changes in *a* and *c* relative to the orthorhombic (Pna2_1) structure. (green spheres represent group Ga cations, blue spheres represent group Li cations and red spheres represent O anions. Parameters *a, b* and *c* are indicated).

Results

Two-phase equilibrium transformation of LGO from the space group Pna2_1 to I4_1/amd has been investigated. The orthorhombic (Pna2_1) and body-centered tetragonal (I4_1/amd) structures of LGO are shown in Figure 1. In order to estimate the stable crystalline structure under hydrostatic pressure, the common-tangent line will be figure out to indicate transition state under hydrostatic pressure (Wentzcovitch *et. al.*,2007;Sailuam *et. al.*,2017). The results shown that the equilibrium hydrostatic pressure for the phase transformations from the common-tangent lines occurs at around 3.7 GPa.

The result has been shown in Figure 2. The Table 1. also shows the crystal parameters and selected properties at equilibrium phase transition pressure collected from previous work comparable to recent calculations such as the percentage changes in *a* and *c* relative to the orthorhombic (Pna2_1) structure (Δa and Δc ,respectively), bulk modulus (B_0), transformation pressures (P_t) and volume of LGO in Pna2_1 and I4_1/amd structures. The lattice parameters of these structures are consistent with previous theoretical and experimental data. GGA gives the lattice constant of LGO in better agreement with the known experimental value than local density approximation (LDA) XC functional (Perdew & Zunger, 1981) which has been used to study ZnO (Boonchun & Lambrecht, 2010).

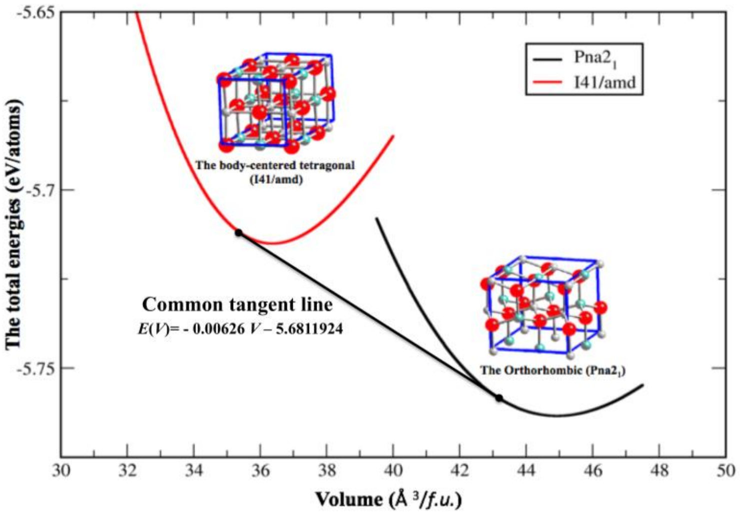

Figure 2 The total energies (eV/atoms) of ternary crystalline structures of LGO in Pna2_1 and I4_1/amd as a function of volume (Å^3/*f.u.*).

Furthermore, the enthalpy surfaces of structures have been calculated for different phase-pairs. The contour plot of the minimized enthalpy is the key important role for further investigation of LGO phase transformations under high pressure as show in Figure. 3. The $\Delta H = H^{I41/amd} - H^{Pna21}$, indicates the relative enthalpy of I4_1/amd with respect to Pna2_1 as a function of lattice parameters. At 3.7 GPa, the hydrostatic compression causes the $Pna2_1$ (four-fold) structure to collapse into the denser phase $I4_1/amd$ (six-fold) structure, with considerable transition energy barrier. The calculation of the contour plot enthalpy at equilibrium transition pressure P_t = 3.7 GPa is shown in Figure.3(a). The plots clearly exhibit the equilibrium pressure at 3.7 GPa where the enthalpy values of both structures are comparable.

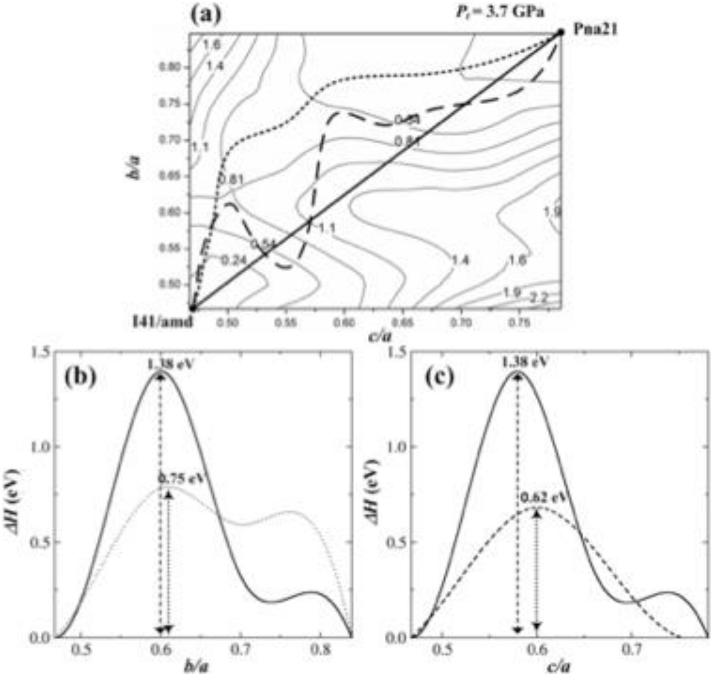

Figure 3 (a) Contour plot of the minimized enthalpy as a function of *c/a* and *b/a* in LGO under the equilibrium transition pressure at P_t = 3.7 GPa. Dotted (dashed) line indicates the parallel (in-plane) strain induced transformation path. Solid line indicates the straight diagonal path. (*b*,*c*) Minimum enthalpy differences ΔH at the equilibrium transition pressure P_t = 3.7 GPa along different paths: dotted line (b), parallel strain induced path; (c), in-line strain induced path; while solid lines represented straight diagonal path.

Table 1 The crystal parameters and selected properties of LGO in Pna2$_1$ and I4$_1$/amd structures at equilibrium phase transition pressure. ΔV, Δa and Δc are the percentage changes in volume, *a* and *c* relative of body-centered tetragonal (I4$_1$/amd) to the orthorhombic (Pna2$_1$) structure.

Phase	*a* (Å)	*b* (Å)	*c* (Å)	*b/a*	*c/a*	*V* (Å^3/*f.u*)	□*V* (%)	□*a* (%)	□*c* (%)	B_0 (GPa)
Orthorhombic (Pna2$_1$)	6.45,	5.48,	5.08,	0.85	0.79	44.93,				80.93,
	6.26[a],	5.36[a],	4.95[a],			41.53[a],				
	6.32[b]	5.38[b]	4.99[b]			42.44[b],				95.69[b]
	6.37[c]	5.40[c]	5.01[c]			43.09[c]				
Body-centered tetragonal (I41/amd)	8.728	4.082	4.082	0.47	0.47	36.36	-19.99,	25.50	19.65	164.79

[a] VASP code DFT- LDA calculation by Boonchun (Boonchun & Lambrecht, 2010)

[b] CASTEP code DFT-LDA calculation by Li (Lei *et.al.*,2013).

[c] Piston and cylinder device by Marezio (Marezio & Remeika,1965).

In Figure 3(a), the 3 transformation paths are presented in form of the multidimentional *c/a-b/a* space, for each *c/a*, any *b/a* those provide the minimum enthalpy were figured out and plotted. Likewise, the dotted line corresponds to the transformation induced by a *b/a* strain (i.e., an in-plane strain (Limpijumnong & Jungthawan, 2004)), any *c/a* where the minimum enthalpy were found has been plotted. The dashed line corresponds to transformation induced by a *c/a* strain, any *b/a* where the minimum enthalpy were found has been plotted.

Discussion

The solid line is straight diagonal path obtained from the relation as [(*b*/*a*)-0.468] = 1.19 [(*c*/*a*)-0.468] equation. The cross sections of the enthalpy surface along all three paths clearly show the homogeneous transformation barrier of Pna2$_1$ to I4$_1$/amd around 0.62 eV to 1.38 eV or 38.75 meV/atoms to 86.25 meV/atoms as shown in Figure. 3 (b and c). The lowest enthalpy barrier is 38.75 meV/atoms. On the other hand, the highest transformation barrier of Pna2$_1$ to I4$_1$/amd is 86.25 meV/atoms along the straight diagonal path. The homogeneous transformation barrier of LGO is twice larger than ZnO, which had been reported by Jungthawan and Limpijumnong (37.50 meV/atom) (Limpijumnong & Jungthawan, 2004). In contrast, the transformations along the dotted and dashed lines exhibit much lower of the energy barriers. It means when the hydrostatic pressure has been applied to the LGO, the energy barrier in parallel (in-plane) is lower than the straight diagonal path. Furthermore, the relaxation in both *b*- and *c*-axis unequally responses in transformation process in LGO under high pressure. This result is consistent with the phenomena that the elasticities in shape tend to occur with higher possibility than the elasticities in length at the equivalent pressure. Furthermore, the unequal relaxation may lead to the cation-disordering as reported in (Hu *et.al.*,2018).

Finally, the tetragonal structure of LGO has been found here at 3.7 GPa while in the experiment this structure has been discovered at 11 GPa (Hu *et.al.*,2018) .Unsurprisingly, the observed transition pressure is larger than the calculated value because of the large kinetic barriers (enthalpy barrier) that obstruct the transition at the equilibrium pressure, dominant to a hysteresis between the forward and backward transitions. The large hysteresis has indeed been observed in transition of binary wurtzite-to-rocksalt phase transformation of ZnO (Limpijumnong & Jungthawan, 2004), SiC (Yoshida *et.al.*,1993) and GaN (Perlin *et.al.*,1992).

Conclusions

The investigation of phase transformations of LGO under high hydrostatic pressure conditions was carried out using ab abinitio calculations. The high-pressure phases of LGO ($I4_1$/amd) have been revealed. The result indicated that hydrostatic pressure induces transformations of the orthorhombic ($Pna2_1$) to the body center tetragonal (BCT, $I4_1$/amd) is 3.7 GPa. Furthermore, the LGO rocksalt-like structure ($I4_1$/amd) exhibits the difference behavior from its ZnO counterpart corresponding to the enthalpy barriers, which is twice larger of ZnO (86.25 meV/atom and 37.50 meV/atom, respectively). The relaxation in both *b*- and *c*-axis unequally responses in transformation process in LGO under high pressure. Ferthermore, the enthalpy in parallel (in-plane) is lower than the straight diagonal path in ternary wurtzite LGO transformation process following B4-B1 of binary compounds.

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