Calculation and Analysis of the Lattice, Electronic Structures, and Dielectric Functions for Monoclinic ZrO$_2$ under High Pressure

Chao Zhang, Ruisong Guo,* Zhichao Liu, Guanglan Cai, Weina Guo, and Chen Wu

Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

(Received January 7, 2015; Revised July 5, 2015)

The pseudo-potential plane wave method and the generalized gradient approximation have been used to calculate the lattice, electronic structures (density of states, band structures, and Mulliken bond population), and dielectric functions of monoclinic ZrO$_2$ under high pressure. Combining the lattice and electronic structures results, the dielectric function imaginary parts (ε$_2$(ω)) have been analyzed with the optical transition theory. These results may be helpful for the dielectric spectrum measurements of monoclinic ZrO$_2$ under high pressure.

DOI: 10.6122/CJP.20150813 PACS numbers: 78.20.Bh

I. INTRODUCTION

Zirconia (ZrO$_2$) possesses a high dielectric constant, a wide optical band gap, an excellent mechanical strength, and high thermal stability [1]. Due to the excellent properties above, ZrO$_2$ has been applied widely in the field of high-k dielectric, high-index film, and structural ceramics [2]. The lattice structure of ZrO$_2$ depends on the temperature and pressure. Under ambient pressure, there are three polymorphs, monoclinic, tetragonal, and cubic as the temperature increases [3]. At ambient temperature, there are phase transitions upon compression [4].

Many theoretical works have been reported on the transient behavior and properties of ZrO$_2$ under high pressure. Dewhurst et al. [5] predicted the transition pressures based on the local density approximation (LDA) method. Ozturk et al. [6] calculated the transition results by means of the generalized gradient approximation (GGA) method. Milman et al. [7] studied the structural, electronic, and vibrational properties of tetragonal zirconia under pressure with density functional theory (DFT). Fadda et al. [8, 9] investigated the structural parameters of several polymorphs of ZrO$_2$ under high pressure using the LDA and GGA methods. They also studied their static dielectric properties under high pressure. However, the optical frequency dielectric properties of ZrO$_2$ under high pressure have rarely been studied in detail. And the detailed change in the electronic structure of ZrO$_2$ under high pressure was also less studied.

*Electronic address: rsguo@tju.edu.cn
In dielectric physics [10], the dielectric properties are closely related to the electronic structures of the material. The relationship between the macroscopic properties and the microscopic structures is very important for material research [11]. The microscopic information can be understood through the dielectric properties measurement. Besides, the electronic structures and the dielectric properties in the range of optical frequency can be calculated by the first principles calculations.

Based on the above, the optical frequency dielectric properties of monoclinic ZrO$_2$ under high pressure have been discussed with relation to the lattice and electronic structures in this work. We hope the results may be helpful for the dielectric spectrum analysis for ZrO$_2$ under high pressure.

II. METHOD OF CALCULATION

The unit cell of monoclinic ZrO$_2$ is chosen as the model in the work. Monoclinic ZrO$_2$ belongs to the $P2_1/c$ space group. The details of the geometrical optimization of ZrO$_2$ are as follows: the Cambridge serial total energy (CASTEP) code was applied, which uses a plane wave expansion technology in reciprocal space. The GGA of the Perdew-Wang (PW91) scheme [12] was used for the exchange-correlation energy calculations. The presence of tightly-bound core electrons was represented by ultrasoft pseudo-potentials of the Vanderbilt type. A special $k$ point sampling method proposed by Monkhorst-Pack was used for the energy integration in the first irreducible Brillouin zone. In the calculation, the kinetic energy cut-off value was selected as 500 eV, which was sufficient to obtain reliable results. The $k$ point mesh was selected as $5 \times 5 \times 5$. All atoms were relaxed to their equilibrium positions when the energy change on each atom between successive steps converged to $5 \times 10^{-6}$ eV/atom, the forces on each atom converged to 0.01 eV/Å, the stress on each atom converged to 0.02 GPa, and the displacement converged to $5 \times 10^{-4}$ Å. Different hydrostatic pressures from 0 to 22 GPa with interval 1 GPa were set in the geometry optimization, in which atomic coordinates are allowed to relax at each pressure.

III. RESULTS AND DISCUSSION

III-1. Lattice parameters of monoclinic ZrO$_2$ under high pressure

The equilibrium lattice parameters calculated for monoclinic ZrO$_2$ under ambient pressure are 5.18 Å for a, 5.23 Å for b, 5.35 Å for c, and 99.58 degree for $\beta$, the results are very close to the experimental data [13, 14] and the reported calculation results [15, 16]. The evolution of the lattice parameters for monoclinic ZrO$_2$ under high pressure is shown in Fig. 1(a).

The lattice parameters for monoclinic ZrO$_2$ decrease as the pressure increases. At about 8 GPa and 12 GPa, the curves display two abrupt changes. This result suggests that there are two phase transitions under high pressure, in agreement with previous experimental data and theoretical reports of the phase transition [6, 17–19].
VOL. 53  CHAO ZHANG, RUISONG GUO, ZHICHAO LIU, ET AL.  120803-3

FIG. 1: (a) Evolution of the lattice parameters under high pressure for monoclinic ZrO$_2$, (b) total energy $E$ as a function of the corresponding volume $V$ in monoclinic ZrO$_2$, (c) total energy $E$ as a function of the pressure $P$ in monoclinic ZrO$_2$, (d) volume $V$ as a function of the pressure $P$ in monoclinic ZrO$_2$.

In addition, the total energy $E$ and the corresponding volume $V$ of the monoclinic ZrO$_2$ unit cell are calculated. The $E - V$ plot is shown in Fig. 1(b). In the figure, there are relatively obvious changes (marked in the figure) of energy and volume at about 8 GPa and 12 GPa. The plots of the energy $E$ vs. the pressure $P$ and the volume $V$ vs. the pressure $P$ are also shown in Fig. 1(c) and Fig. 1(d). There are abrupt changes at about 8 GPa and 12 GPa in both the figures. The $E - V$, $E - P$, and $V - P$ plots also shows the phase transitions under high pressure.

III-2. Densities of states and band structures under high pressure

Fig. 2 shows the densities of states (DOS) for the Zr state, O state, and monoclinic ZrO$_2$ under different pressures. There is strong hybridization between the Zr and O orbitals, which indicates that the Zr and O atoms could form covalent bonds with each other. As
the pressure increases, the DOS peaks for ZrO$_2$ become dispersed and obvious in the energy range from $-6$ to $0$ eV. The DOS peaks shift to a high energy in the energy range from $3$ to $11$ eV. And in this energy range the numbers of the DOS peaks increase. The results can be explained by the fact that higher pressure makes the distance of the atoms of monoclinic ZrO$_2$ become smaller in general. This leads to stronger interactions among the atoms. The stronger interaction makes the energy level splitting [20]. The energy level splitting makes the DOS peaks become dispersed and obvious. The results above are also observed from the DOS curves for the Zr and O states.

**FIG. 2:** Densities of states for the Zr state, O state, and monoclinic ZrO$_2$ under different pressures.

Furthermore, the detailed change of the DOS of monoclinic ZrO$_2$ under pressure is shown in Fig. 3. As pressure increases, the DOS curve changes slightly, except for the DOS curve of 8 and 12 GPa. There is an obvious change in the DOS curve when the pressure is 8 and 12 GPa. This result indicates that a phase transition can be reflected by the obvious change in the DOS curves. Fig. 4 shows the band structures of monoclinic ZrO$_2$ under pressure. The bottom of the conduction band shifts to higher energy with the increasing pressure, while the top of the valance band has no obvious changes. This result can be reflected by the mentioned fact that the DOS peaks shift to a higher energy in the energy range from 3 to 11 eV.

**III-3. Mulliken bond populations analysis**

According to the symmetry of the lattice, there are seven kinds of Zr-O bonds in monoclinic ZrO$_2$. The seven bonds are marked in Fig. 5(a). In the figure, the six bonds marked by solid lines are in the unit cell of monoclinic ZrO$_2$, and one bond marked by a dashed line is between two unit cells. Fig. 5(b) shows the evolution of the Mulliken
FIG. 3: Local DOS curve for monoclinic ZrO$_2$ under different pressures (the red square frame shows the obvious change of the DOS curve).

FIG. 4: Band structures of monoclinic ZrO$_2$ under different pressures.
bond populations of Zr-O bonds under pressure. All the Mulliken bond populations of the Zr-O bonds are above zero, which indicates that the Zr and O atoms must form covalent bonds with each other. The red squares show the obvious change of the Mulliken bond populations. The corresponding pressures of the square are about 8 and 12 GPa, which reveals that the phase transition can be reflected by the obvious change in the Mulliken bond population of the Zr-O bounds. In addition, the bond lengths of the Zr-O bonds are also calculated and shown in Fig 5(c)–5(i). The obvious changes are marked by a red square. The corresponding pressures of the square are also about 8 and 12 GPa, which reveals that the phase transition can be reflected by the obvious change in the bond lengths of the Zr-O bounds. In addition, some Zr-O bond lengths increase and some others decrease as the pressure increases. This may be explained by the changes of the lattice constants not being proportional to that of the pressure in Fig. 1.

III-4. Dielectric functions analysis

The real part ($\varepsilon_1$) and the imaginary part ($\varepsilon_2$) of the dielectric function are shown in Fig. 6(a) and Fig. 6(b) for monoclinic ZrO$_2$ under different pressures. In Fig. 6(a) and Fig. 6(b), there are normal and abnormal dispersions appearing in the dielectric functions, which are consistent with the dielectric theory [11]. So the calculations are reliable in this paper. Optical properties can be determined using the complex dielectric function as follows:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega).$$

(1)

In Fig. 6(b), the positions of the $\varepsilon_2(\omega)$ peaks are related to the transitions between the conduction and valence bands [10]. Combining the DOS calculation results (Fig. 2), in the energy below 19 eV, the transitions have been taken into account from the O state to the Zr state. In Fig. 6(b), the $\varepsilon_2(\omega)$ peaks shift to higher energy as pressure increases. This can be explained as follows: the DOS peaks of the Zr states in the energy range from 3 to 11 eV (this energy range belongs to the valence band energy) shifts to a higher energy as pressure increases. In addition, the band gap between the conduction and valence band in Fig. 2 increases as pressure increases. Thus, the transition energy increases, leading to the $\varepsilon_2(\omega)$ peaks existing in the high energy range.

Besides, the $\varepsilon_2(\omega)$ curve below 19 eV actually includes two peaks in Fig. 6(b). When the pressure increases, the two peaks become dispersed and obvious. This can be explained by noting that the DOS peaks for the Zr and O states become dispersed and obvious as the pressure increases. According to the optical transition theory in solid state physics [21, 22], the value of $\varepsilon_2(\omega)$ is proportional to the integration of the transition probability between the conduction and valance band. The transition probability between the DOS peaks is large. The dispersed and obvious DOS peaks will lead to dispersed and obvious $\varepsilon_2(\omega)$ peaks.

Furthermore, the following formula from [10, 21] is considered:

$$N(\omega) = \frac{2m\varepsilon_0}{\varepsilon^2 \pi} \int_0^\omega \omega \varepsilon_2(\omega) d\omega,$$

(2)
FIG. 5: (a) Seven bonds in monoclinic ZrO$_2$, (b)–(i) Mulliken bond populations and bond lengths for the Zr-O bonds under different pressures.

where $N$ is the density of electrons participating in the transition, $m$ is the electronic mass, $\varepsilon_0$ is the vacuum dielectric constant; we calculated $N(\omega)$ of monoclinic ZrO$_2$ under different pressures as Fig. 7 shows.

In Fig. 7, the $N$ value at 20 GPa is the largest in general, and the value at 0 GPa is the smallest. So there are the most electrons taking part in the transition, which indicates that the transition probability is the largest at 20 GPa. It can be explained with the DOS curves of the O state under different pressures (Fig. 2). The transitions mentioned above are all from the O state in valence bands to other state. The O-p state density curve at 20 GPa spans the vastest energy range. Comparing the same situations at 0 GPa and 20 GPa, the transition probability at 20 GPa is the largest, leading to the largest value of the
FIG. 6: The real part (a) and the imaginary part (b) of the dielectric functions of monoclinic ZrO$_2$ under different pressures.
FIG. 7: Density of electron participating in the transition for the energy.

The result reveals that the value of the $\varepsilon_2(\omega)$ curve is influenced by the energy range which the state density curve spans.

Fig. 8 shows the detailed change of the imaginary part of the dielectric functions of monoclinic ZrO$_2$ under different pressures. As pressure increases, the $\varepsilon_2(\omega)$ curve changes slightly except for the DOS curve of 8 and 12 GPa. There is an obvious change in the $\varepsilon_2(\omega)$ curve when the pressure is 8 and 12 GPa. This result indicates that the phase transition can be reflected by an obvious change in the DOS curves.

IV. CONCLUSIONS

The lattice constants of monoclinic ZrO$_2$ possess nonlinearity changes with pressure. When the pressure is 8 GPa or 12 GPa, the lattice constants have abrupt changes. The DOS and Mulliken bond populations have been calculated under different pressures. The results show that: there is an abrupt change in the DOS and Mulliken bond populations under 8 GPa or 12 GPa. The results of the electronic structures observation are due to the changes of the lattice constants.

The dielectric functions have been calculated, which indicates that: the calculations are in accordance with the dielectric theory on the appearance of normal and abnormal dispersions; there are internal relations among the imaginary part $\varepsilon_2(\omega)$ curve, the distribution of the DOS curve, and the Mulliken bond populations. Much information on the electronic structure can be learned from the macroscopic $\varepsilon_2(\omega)$ curve obtained from the dielectric experiment. The dielectric functions which can be obtained by experiments are
determined and influenced by the DOS and Mulliken bond populations; in other words, the electronic structure of the elements holds the key to understanding the relationship between the composition, atomic arrangement, and properties. These results would be helpful for the dielectric measurement and analysis of monoclinic ZrO$_2$.

**Acknowledgements**

The authors are grateful for the support of the Tianjin Natural Science Foundation (Grant No. 14JCYBJC17000) and National Natural Science Foundation of China (Grant No. 51372165).

**References**


