



Vibrational and elastic properties as a pointer to stishovite to CaCl₂ ferroelastic phase transition in RuO₂



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ABSTRACT

The high pressure behavior of RuO₂ has been investigated using the first principles calculations based on the density functional theory. Here, we report the calculated properties on structure, electronic, elastic, phonon and electron–phonon coupling of rutile and CaCl₂ type RuO₂. Our calculated lattice constants and bulk modulus agree reasonably well with the available theoretical and experimental data. Results of our calculations of zone center phonon modes at ambient and high pressures are in good agreement with Raman scattering measurements. Elastic (shear) modulus and phonon analysis confirm the ferroelastic phase transition from rutile to CaCl₂ phase in RuO₂. It is clearly illustrated that the first transition is associated with macroscopic shear instability which arises from the strong coupling between elastic constants and softening of Raman active B_{1g} mode. The observed pressure of phase transition in experimental measurements was reproduced more accurately than in previous calculations and the difference between observed and calculated transition pressure is only of the order of few percentage. We have also analyzed the rotation angle for O–R–O corresponding to B_{1g} mode and found that the rotation of bond about 8° is required for transition from rutile to CaCl₂ phase in RuO₂. In addition, the mode Grüneisen parameter is discussed. The electron–phonon interaction in both rutile and CaCl₂ type RuO₂ at high pressure is also discussed.

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1. Introduction

Ruthenium dioxide (RuO₂) is one of the most important materials having the rutile structure at ambient condition. Its low resistivity and reactivity has long been known and found importance in industrial applications as potential electrode materials for high energy-density storage (electrochemical) capacitors, a catalytic agent, a striplike conductor in integrated circuits and a diffusion barrier in contact metalization (Pedder, 1976; Kolowa et al., 1987; Krusin-Elbaum et al., 1987; Glassford and Chelikowsky, 1994; Krasovska et al., 1995; Zhen and Jow, 1995).

Further, interest in RuO₂ stems from its structural similarity to stishovite (SiO₂), a geological important mineral and high pressure polymorphs of silica appearing in the lower mantle of the Earth and undergoes the orthorhombic denser CaCl₂ type structure (Haines and Léger, 1997; Haines et al., 1995, 1996; Nagel and O'Keefe, 1971; Hazen and Finger, 1981; Kingma et al., 1995; Haines et al., 2000; Ono et al., 2002; Hellwig et al., 2003). Several AO₂ rutile type compounds have been found to undergo

structural transformations to an orthorhombic CaCl₂ type structure (Nagel and O'Keefe, 1971; Hazen and Finger, 1981; Kingma et al., 1995; Haines et al., 2000; Ono et al., 2002; Hellwig et al., 2003; Carpenter et al., 2000), which is very closely related to the rutile structure. In both structures, the cation is octahedrally coordinated by the anions, forming chains of edge sharing octahedral along the 'c' axis and, two octahedral connected by sharing one corner. The symmetry of rutile type structure is tetragonal, with two formula units per cell ($Z = 2$) having a spacegroup P4₂/mnm. The symmetry of the CaCl₂ type structure is orthorhombic having spacegroup Pnmm with two formula units per cell ($Z = 2$), which is a direct subgroup of P4₂/mnm. This direct group–subgroup connection clearly indicates the pronounced possibility of a second order ferroelastic phase transition driven by B_{1g} Raman active optical phonon mode which is an active representation of zone center of the Brillouin zone and referred as the order parameter (Q) (Hellwig et al., 2003; Anderson, 1960; Landau and Lifshitz, 1961; Cochran, 1960). This order parameter describes the rotation of the RuO₆ octahedra within the (001) plane and is Raman active. In the ferroelastic phase transition, the transverse acoustic soft mode can also to be referred as direct order parameter or couple bilinearly order parameter. While

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in the first case the phase transition is driven by B_{1g} Raman active phonon mode and is called pseudoproper ferroelastic phase transition, the driving force in the second case is the elastic instability and is called proper ferroelastic. The acoustic soft modes, which describe the elastic instability, follow the bilinear coupling to the order parameter. However, the Raman active B_{1g} mode, which softens in the rutile phase, has A_g symmetry in the CaCl_2 phase (Hellwig et al., 2003).

Because of the above mentioned interest in high pressure behavior of metal dioxides and the lack of adequate understanding of the mechanism from the rutile to CaCl_2 type transition, the last few years have witnessed both the experimental and theoretical predictions of high pressure behavior of ruthenium dioxide (Haines and Léger, 1993, 1997; Rosenblum et al., 1997; Ono and Mibe, 2011; Wu and Weber, 2000). However, the conclusion concerning the mechanism including the phase transition pressure diverges. There exist even the difference of about 70 cm^{-1} for most important phonon mode, B_{1g} in rutile RuO_2 in two Raman measurements (Rosenblum et al., 1997; Huang and Pollak, 1982). The earliest study on RuO_2 at high pressure was performed using x-ray powder diffraction technique by Haines and Léger (1993) and predicted 5 GPa as transition pressure for rutile to CaCl_2 phase transformation at room temperature. Neutron diffraction study by Haines et al. (1997) showed this rutile to CaCl_2 phase transition in RuO_2 at 5.3 GPa. These were followed by the high pressure Raman spectroscopic study which, in contrast, predicts the transition pressure as $11.8 \pm 0.3 \text{ GPa}$ (Rosenblum et al., 1997), more than double of the x-ray and neutron diffraction predictions (Haines and Léger, 1993; Haines et al., 1997). The ab-initio calculation, using the full potential linearized augmented plane wave (FLAPW) method, predicts this transition pressure as 24–27 GPa (Wu and Weber, 2000), which is quite high in comparison to the available experimental data. More recently, Ono and Mibe (2011) have performed the in situ high pressure and high temperature Raman spectroscopy with an objective to determine the accurate phase transition pressure for rutile to CaCl_2 type structural phase transition in RuO_2 . They observed a value of phase transition pressure of 7.6 GPa in between the two other experimental findings: x-ray diffraction (Haines and Léger, 1993) and Raman spectroscopy (Rosenblum et al., 1997), which they attributed to the experimental constraints and nature of the phase transition. However, none of the experimental findings (Haines and Léger, 1993; Haines et al., 1997; Rosenblum et al., 1997; Ono and Mibe, 2011) is close to the ab-initio calculation (Wu and Weber, 2000). In addition, the discrepancy in ab-initio calculation can be due to not involving the optimization of all structural parameters at all considered pressures (Karki et al., 1997; Tsuchiya et al., 2004; Gupta et al., 2013). Therefore, in order to understand in detail the pressure induced structural behavior, particularly the phase transition in rutile RuO_2 and settle the issue of existing controversies among the experimental and theoretical predictions of the structural phase transition in RuO_2 , further high pressure studies mainly using ab-initio calculations are essential. The predictive power of first-principles calculations in ground state configurations, large set of different phases and structural changes as a function of pressure is well recognized for rutile type metal dioxides.

In metal dioxides, the phonon dispersion curves are very important particularly in light of pressure effects. Though Raman spectroscopy has been used to identify the phase transition in RuO_2 , there is not a single study on the pressure dependent lattice dynamical properties for this compound using theoretical calculations, mainly the first principles ab-initio calculations. The lattice dynamical calculations with pressure have always been useful in understanding the mechanism of phase transition and identifying the responsible phonon mode(s).

In this paper, theoretical results from ab-initio calculations on lattice dynamical properties for rutile and $\text{CaCl}_2\text{-RuO}_2$ at pressure up to 14 GPa are reported. Here, we use an efficient full structural optimization i.e. optimization of all structural parameters (lattice constants and free ionic positions) (Karki et al., 1997; Tsuchiya et al., 2004; Gupta et al., 2013). The main objective of the present work is to determine the phase transition pressure between the rutile and CaCl_2 structures and elucidates the inconsistency in transition pressures obtained from different studies. Furthermore, a detailed study of RuO_2 analogous to silica an important component of the Earth's mantle would make a valuable contribution to the understanding of the transition of silica polymorphs. The paper also reports electronic band structure at different pressures and pressure dependent electron-phonon (e-p) coupling and superconducting transition temperature.

The organization of the paper is as follows: In Section 2, we describe the computational details for calculating the structural, elastic and lattice dynamical properties. Section 2 also reports the electronic band structure and electronic density of states. Section 3 presents the results and discussions on calculated properties. Finally, Section 4 concludes our findings of the present study.

2. Computational details

We have performed the ab-initio total energy calculations within the density functional theory (DFT) (Hohenberg and Kohn, 1964) using the plane wave method and pseudopotentials theory with the quantum espresso ab-initio simulation package (Giannozzi et al., 2009). The description of the exchange correlation energy was described with the local density approximation (LDA) parameterized by Perdew and Zunger (1981) within ultrasoft pseudopotentials build by Vanderbilt pseudopotentials scheme (Vanderbilt, 1990). A plane-wave basis set with a 50 Ry cutoff was used to expand the electronic wave functions at the special k -points generated by a $6 \times 6 \times 9$ Monkhorst-pack grid in the Brillouin zone where the integrations are carried out by the Methfessel-Paxton smearing techniques using with shift from origin (Methfessel and Paxton, 1989). The final plane-wave basis set corresponds to total energies and stress differences converged to 0.01 meV and 0.01 GPa per unit formula. A Broyden-Fletcher-Goldfarb-Shanno (BFGS) (Bonnans et al., 2006) algorithm was used to relax electrons, ions and cell parameters of the unit cell. The second order elastic constants are calculated using the numerical differentiation of physical stress of a crystal as a function of the imposed strain. To calculate the second order elastic constants the optimized geometry has been considered in terms of both cell parameters and atomic positions, where the equilibrium configurations is used as reference system. The second order derivative of the stress has been calculated from the 5 sets of deformed crystal structures created using the knowledge of the space group number. Finally for the each deformed structure, the internal degrees of freedom are again optimized. Phonon calculations were performed using the density functional perturbation theory (DFPT) (Baroni et al., 2001). The advantage of DFPT linear response method is that it allows calculations for the phonons at any wave vector only using unit cell. The dynamical matrices were calculated on $(2 \times 2 \times 3)$ grid (q -points) sampling where all the structural parameters were fully relaxed.

3. Results and discussion

3.1. Structural properties

At a first step the structural optimization of rutile and CaCl_2 type RuO_2 has been performed under the minimum condition of

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