First Principles Study of Structural and Elastic Properties of BaWO$_4$ Scheelite Phase Structure under Pressure
A. Benmakhlouf, A. Bentabet

Abstract—In this paper, we investigated the athermal pressure behavior of the structural and elastic properties of scheelite BaWO$_4$ phase up to 7 GPa using the ab initio pseudo-potential method. The calculated lattice parameters pressure relation have been compared with the experimental values and found to be in good agreement with these results. Moreover, we present for the first time the investigation of the elastic properties of this compound using the density functional perturbation theory (DFPT). It is shown that this phase is mechanically stable up to 7 GPa after analyzing the calculated elastic constants. Other relevant quantities such as bulk modulus, pressure derivative of bulk modulus, shear modulus; Poisson’s ratio, anisotropy factors, Debye temperature and sound velocity have been calculated. The obtained results, which are reported for the first time to the best of the author’s knowledge, can facilitate assessment of possible applications of the title material.

Keywords—Pseudo-potential method, pressure, structural and elastic properties, scheelite BaWO$_4$ phase.

I. INTRODUCTION

Both CaWO$_4$ and PbWO$_4$ are promising materials for the next generation of cryogenic phonon-scintillation detectors [1]-[3]. This has motivated a renewed interest on the fundamental physical properties of the AWO$_4$ tungstates (with A = Ca, Sr, Ba, Pb, Eu) which under normal conditions crystallize in the tetragonal scheelite structure [4].

The scheelite tungstates are in fact technologically important materials used during the last years as solid-state scintillators [5]-[7] and in other optoelectronic devices [8]-[10]. In the last few years, the barium tungstate BaWO$_4$, crystal with a Scheelite structure, has attracted interests of several research groups due to his applications as laser host material, scintillator in high-energy physics detectors and oxide ion conductor [11]. Among the tungstate materials, BaWO$_4$ is a potential material to be a universal Raman-active crystal [12]-[14]. Structurally, under compression, BaWO$_4$ exists in several forms, such as scheelite, wolframite, fergusonite and HgMoO$_4$ [15]-[17]. At ambient conditions up to 7GPa, it’s known to exist in the scheelite structure, Fig. 1. The scheelite crystal structure is characterized by the tetragonal space group $I4_1/a$ listed as No. 88 in the International Tables of Crystallography, with a number of formula units per cell $Z=4$ [4]. In this structure, the primitive unit cell has two ABX$_4$ units. The scheelite crystal structure can be described as highly ionic with $A^{2+}$ cations and tetrahedral $BX_4^{-2}$ anions. Each B site is surrounded by four equivalents X sites in tetrahedral symmetry and the tetrahedral $BX_4^{-2}$ anions have short B-X bond lengths, which are quite rigid even under compression [18].

The goal of the present study is to examine comprehensively the effect of pressure on the structural and elastic properties of the scheelite crystal BaWO$_4$ up to 7GPa in order to help understand and control the material properties under stress. The rest of the paper has been divided in three parts. In Section II, we briefly describe the computational techniques used in this study. The most relevant results obtained for the structural and elastic properties of the BaWO$_4$ crystal are presented and discussed in Section III. Finally, in Section IV we summarized the main conclusions of our work.

Fig. 1 $1 \times 1 \times 1$ Unit cell of BaWO$_4$ tetragonal structure (scheelite) at ambient conditions. The W atoms are tetrahedrally coordinated to oxygen.

II. COMPUTATIONAL METHOD

Theoretical calculations were performed by employing pseudo-potential plane–wave (PP-PW) method as implemented in the CASTEP (Cambridge Serial Total Energy Package) code [19]. Interactions of valence electrons with ion cores were represented by the Vanderbilt-type ultra-soft pseudo-potential [20]. The exchange-correlation potential was calculated by the generalized gradient approximation (GGA) based on Perdew Wang (PW91) [21]. The PW91 is widely used in DFT. Moreover, several density functions, such as PBE, RPBE and LDA, have been tested in the calculations of electronic structures and optical properties for the PbWO$_4$ and CaMoO$_4$ crystal. The calculated results using the PW91 are more close to the experimental results. The structure of

---

A. Benmakhlouf is with the Département de Physique, Faculté des Sciences Exactes, université Abderrahmane Mira – Bejaia, Algérie and is with the Laboratoire de Physique des Matériaux, Université Amar Telidji de Laghouat; BP 37G, Laghouat 03000, Algerie (corresponding author to provide phone: 0555153835; e-mail: benmakhlouf_ab@yahoo.fr).

A. Bentabet is with Laboratoire de Recherche : Caractérisation et Valorisation des Ressources Naturelles, Université de Bordj Bou Arreridj, 34000, Algérie.
**BaWO₄** is similar to PbWO₄ and CaMoO₄ crystal [12]. So they must be the similar properties and the PW91 is selected in this paper. In addition, there are many successful calculations using PW91 [22], [23].

To ensure highly converged and precise results, the integration over the Brillouin zone was done over a 6 × 6 × 4 Monkhorst–Pack grid [24]; the kinetic energy cutoff was set to 700 eV. The equilibrium lattice constant and positional parameters are determined from the global minimum energy. The structural parameters were determined using Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique [25]. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 5 × 10⁻⁷ eV/atom.

### III. RESULTS AND DISCUSSION

#### A. Equilibrium Structural and Elastic Properties

In this work, the initial crystal structure has been built based on the experimental crystallographic data of scheelite phase [26]. To optimize the geometry structure, the ions were relaxed until the Hellman–Feynman forces were below 0.01 eV Å⁻¹ and the cell parameters were relaxed until total stress were below 0.02 GPa. The calculated equilibrium lattice parameters are shown in Table I along with the available experimental and theoretical values for comparison. Our obtained results are in good agreement with the corresponding measured one. The relative differences between the calculated and experimental values of the lattice parameters d(%) = (calculated value – measured value)/ (measured value) are smaller than ±1.4%. This good agreement serves as a proof of reliability and accuracy of the used theoretical method.

<table>
<thead>
<tr>
<th>C11</th>
<th>C33</th>
<th>C44</th>
<th>C66</th>
<th>C12</th>
<th>C13</th>
<th>C16</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.66</td>
<td>78.91</td>
<td>26.87</td>
<td>32.86</td>
<td>46.4</td>
<td>39.45</td>
<td>9.96</td>
</tr>
</tbody>
</table>

| TABLE II | ELASTIC CONSTANTS [GPa] OF BaWO₄ TETRAGONAL STRUCTURE AT ZERO PRESSURE |

The obtained values of the above-mentioned macroscopic elastic parameters are listed in Table III.

Like the elastic constant tensor, the macroscopic elastic parameters, bulk modulus B and shear modulus G, contain information regarding the hardness of a material with respect to various types of deformation. The bulk modulus is much more facile to determine experimentally (by using Birch–Murnaghan equation [32]) than the elastic constant tensor. Alternatively, the bulk and shear moduli are also related to the elements of the elastic constant via the Voigt–Reuss–Hill approach [33]-[35]. Table I provides the calculated Bulk modulus B₀ at zero pressure along with available experimental data. Our results are in a good agreement with values given by experience. The Young’s modulus E, which measures the stress strain ratio in the case of tensile forces and the Poisson’s ratio ν, which is defined as the negative value of lateral (or transverse) strain to the longitudinal strain under uniaxial stress and no volume change [36], are given by [31].

\[
E = \frac{3B_0G}{3B_0+2G} \tag{2}
\]

\[
\nu = \frac{3B_0-2G}{2(3B_0+G)} \tag{3}
\]
The ratio of bulk modulus to shear modulus, \(B_0/G\), is proposed as a criterion to distinguish between ductile and brittle characters of a solid. According to the empirical formula of Pugh [37], a material is brittle (ductile) if the \(B_0/G\) ratio is less (greater) than 1.75. The obtained value of the \(B_0/G\) ratio in the present work is equal to 2.24, which predicts BaWO\(_4\) to be a ductile material.

The value of Poisson’s ratio is indicative of the degree of directionality of the covalent bonds. This value is small (\(\nu = 0.1\)) for covalent materials, whereas for the ionic materials a typical value of \(\nu = 0.25\) [31]. As shown in Table III, the calculated Poisson’s ratio is about 0.30 for BaWO\(_4\). Therefore, the ionic contribution to the interatomic bonding is dominant, which agree with the results given in references [18], [38], [39].

The shear anisotropic factors in different crystallographic planes provide a measure of the degree of anisotropy of atomic bonding in different planes. A value of unity means that the crystal exhibits isotropic properties while values other than unity represent varying degrees of anisotropy. From the elastic constants, we obtain the shear anisotropic factors given for a tetragonal structure by [31].

\[
A_1 = A_2 = \frac{4c_{14}}{c_{11} + 2c_{13} - 2c_{12}}; \quad A_3 = \frac{2c_{14}}{c_{11} - c_{13}} \tag{4}
\]

For the (100), (010) and (001) planes, respectively. The calculated values are as follows: \(A_1 = A_2 = 1.20\), and \(A_3 = 1.31\), this indicates that the elastic properties of the structure are highly anisotropic in the 3 directions.

**TABLE III**

<table>
<thead>
<tr>
<th>(B)</th>
<th>(G)</th>
<th>(E)</th>
<th>(v)</th>
<th>(B_0/G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaWO(_4)</td>
<td>56.54</td>
<td>56.03</td>
<td>56.28</td>
<td>25.11</td>
</tr>
</tbody>
</table>

Once we have calculated the bulk modulus, the shear modulus \(G\) and the Young’s modulus \(E\), we may obtain the Debye temperature, which is an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperature the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. We have calculated the Debye temperature \(\theta_D\) based on the elastic constants using the following common relation [40],

\[
\theta_D = \left(\frac{\hbar}{K_B N_A} \right)^{1/3} \left(\frac{3n}{4\pi M} v_m\right)^{1/3} \tag{5}
\]

where \(v_L\) and \(v_T\) are the longitudinal and transverse elastic wave velocities, respectively. They can be obtained from Navier’s equations [40].

\[
v_L = \frac{\alpha L}{\rho}, \quad v_T = \frac{\alpha T}{\rho} \tag{7}
\]

The calculated sound velocities and Debye temperature as well as the density of BaWO\(_4\) scheelite structure at zero pressure are given in Table IV. Unfortunately, there are no theoretical and experimental results to be compared with them.

**TABLE IV**

| \(\rho\) (in Mg/m\(^3\)), \(v_L\), \(v_T\), \(\theta_D\) for the BaWO\(_4\) Scheelite Structure at Zero Pressure |
|---|---|---|---|---|
| BaWO\(_4\) | 3021.51 | 2018.23 | 3055.77 | 253.99 | 6.16 |

**B. Structural and Elastic Properties under Pressure**

In order to show how to behave the structural parameters under pressure, the equilibrium geometries of BaWO\(_4\) scheelite structure unit cell were computed at fixed values of applied hydrostatic pressure in the range from 0 to 7 GPa, where, at each pressure, a complete optimization for lattice constants is performed. Pressure dependence of the lattice parameters is shown in Fig. 2. We clearly observe a quadratic dependence in all curves of this compound in the considered range of pressure. The solid curve is quadratic least squares fit. The values of linear and quadratic pressure coefficients for the lattice parameter of this structure are given in Table VI together with experimental results of other authors. The present results agree well with the previous experimental values reports for this material [15]. This result shows the power of this method to describe the behavior of a structure under pressure and gives confidence in the predicted results.

**TABLE V**

| \(P\) (GPa), \(\alpha_L\), \(\alpha_T\), \(c_0\), \(c_1\), \(c_2\) for the BaWO\(_4\) Scheelite Structure |
|---|---|---|---|---|---|
| This work | 5.6874 | 0.0275 | 9.429 | 10\(^{-4}\) | 12.842 | 10\(^{-4}\) | 19.10 | 10\(^{-8}\) |
| Exp.[15] | 5.6257 | 0.0276 | 6.929 | 10\(^{-4}\) | 12.749 | 10\(^{-4}\) | 20.02 | 10\(^{-8}\) |

Pressure dependences of the normalized lattice parameters (a/a\(_0\) and c/c\(_0\)), normalized unit cell volume (V/V\(_0\)) (where a\(_0\), c\(_0\) and V\(_0\) are zero pressure equilibrium structure parameters) are illustrated in Fig. 3.

It is shown that, as pressure increases, the normalized lattice parameter c/c\(_0\) decreases more rapidly than the normalized lattice parameters a/a\(_0\), which indicates that the c-axis is more compressible than the a- and b-axes. These results imply that the atomic bonds along the a- and b-directions between nearest neighbors are stronger than those along the c-direction.
As it is shown in Fig. 3, the volume of the unit cell decreases about at 9% and at 7 GPa of its initial value at zero pressure.

Fig. 2 (a) The lattice constant pressure relation (a–P); the solid line is a quadratic least squares fit: a(p) = a0 + a1 p + a2 p^2; (b) The lattice constant pressure relation (c–P); the solid line is a quadratic least squares fit: c(p) = c0 + c1 p + c2 p^2; (c) Evolution of volume under pressure

Fig. 3 Pressure dependence of the normalized lattice constants (a/a0 and c/c0), normalized unit cell volume (V/V0) (where a0, c0 and V0 are zero pressure equilibrium structure parameters) in BaWO4 Scheelite phase

From the present work, we further obtain information on bond compressibility (see Fig. 4). In particular, under hydrostatic conditions, the W-O short distance is 7% less compressible than the Ba-O distance. A similar qualitative behavior is found by [17] which gives the value of 10%. For scheelite BaW04 structure, the first neighbor W-O distances is more rigid than the Ba-O ones. As a consequence, the volume change of BaO8 dodecahedra is larger than that of WO4 tetrahedra.

Now we are interested to study the pressure dependence of the elastic properties. The first principle studies based on DFT can be used to obtain reliable elastic properties of compounds. Several methods are available for computation of stiffness coefficients, but currently the ‘stress–strain’ method seems to be most commonly used and this is the method implemented in CASTEP. In this approach, the ground state structure is strained according to symmetry dependent strain patterns with varying amplitudes and a subsequent computing of the stress tensor after a re-optimization of the internal structure parameters, i.e., after a geometry optimization with fixed cell parameters. The elastic stiffness coefficients are then the proportionality coefficients relating the applied stress to the computed strain [42].

Fig. 4 Pressure dependence of the interatomic bond distances (a) and bond length ratio Ba-O and W-O (b) in the Scheelite phase structure BaWO4

In Fig. 5, we present the variation of the elastic constants (Cij), the bulk modulus B, the shear modulus G and the Born’s criteria for tetragonal crystal [30] of BaWO4 in scheelite phase, with respect to the variation of pressure. We clearly observe a linear dependence in all curves of elastic constants and bulk modulus of this crystal in the considered range of pressure. In Table VI, we listed our results for the pressure derivatives ∂Cij/∂P and ∂B/∂P. It is easy to observe that the elastic constants Cij increase when the pressure is enhanced in this crystal, and satisfy the Born’s criteria (Fig. 5 (c)) indicating that scheelite phase BaWO4 compound is mechanically stable up to 7 GPa. This result is confirmed by other experimental ones [15]-[17]. The calculated pressure derivative B’ = ∂B/∂P is given in Table I with other theoretical and experimental data for comparison. The results of our work agree well with the previous theoretical and experimental reports for this material. To our knowledge, no experimental or theoretical data for the pressure derivative of elastic constants of these compounds are given in the literature. Then, our results can serve as a prediction for future investigations.

<table>
<thead>
<tr>
<th>TABLE VI</th>
<th>CALCULATED PRESSURE DERIVATIVES FOR THE ELASTIC MODULUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,693</td>
<td>3.955</td>
</tr>
</tbody>
</table>
iv. The calculated structural parameters at ambient pressure of this compound are in a good agreement with the available experimental and theoretical data, validating the method used in present work.

v. The elastic constants, Debye temperature and sound velocity are calculated at zero pressure for the BaWO₄ scheelite compound.

vi. We calculated results for the pressure dependence of the structural parameters shows a quadratic dependence in all curve of this compound in the considered range of pressure.

vii. For scheelite BaWO₄ structure, the first neighbor W-O distances is more rigid than the Ba-O ones.

viii. We have found a linear dependence of bulk modulus and elastic constants with applied pressure.

ix. We are not aware of any experimental or theoretical data for the elastic constants and pressure dependence of this compound, so our results may be considered as reliable predictions of the pressure dependence of the elastic properties in this material.

REFERENCES


