Pressure-Induced Layered Structure in BaWO$_4$

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Abstract. We have theoretically investigated the structural stability of the predicted polar phase on the layered Tungsten-based oxide BaWO$_4$ at high pressure. Although the energy vs. volume curves report a non-centrosymmetric Cmc$_2$1 phase in BaWO$_4$ oxide under pressure, we found that such a phase is dynamically unstable when the phonon-dispersions are considered. Additionally, we have observed that the polar eigendisplacements, related to WO$_6$ octahedral rotations, are destroyed once the internal coordinates are allowed to fully relax. Thus, the symmetry of the crystalline material is transformed into a Cmcm phase, where we found a dynamically stable layered structure.

1. Introduction:
Interestingly, layered Ba$MF_4$ fluorides have been highlighted as potential multiferroics and multifunctional materials with a very high Curie temperature, that in most of the cases, lies above 1000 K [1, 2, 3]. Unfortunately, the experimental synthesis process for such materials is quite expensive and dangerous due to the fluorine’s management at the laboratory. Then, counterparts within the oxide’s family, ABO$_4$, might be ideal candidates for such applications. Nevertheless, very few oxide materials within the ABO$_4$ stoichiometric relationship are known.

Recently, experimental and theoretical reports claiming for the existence of a polar structure [4, 5, 6], among other phases [7, 8, 9], as a function of applied hydrostatic pressure in the BaWO$_4$ material. In the field of octahedrally coordinated materials, pressure-induced layered phases have also been observed before in another fluorides and oxides compounds such as NaMnF$_3$ [10] and CaRhO$_3$. The latter showing interesting noncollinear magnetic properties [10, 11]. Thus, high-pressure synthesis route can be used and tuned in order to crystallize this type of layered materials.

On the side of multifunctional related properties, the existence of a polar stable state in these layered materials suggests the possible entanglement of the spontaneous polarization with a large spin-orbit coupling, SOC, coming from the 4$d$ and 5$d$ cations present in the structure. Therefore, these conditions, possibly present at BaWO$_4$, could give rise to the control of spin-splitting through the Rashba and Dresselhaus effects [12, 13]. Such type of coupling in this type of materials, and mainly, in the W-based compounds, will be stronger due to the rather large SOC when comparing with similar transition metal elements. Furthermore, the Tungsten’s oxidation state, i.e. +6 in the BaWO$_4$, increases the spin-orbit coupling strength [14] making it a perfect candidate for such applications. Therefore, the confirmation and study of the polar...
state in this, or similar compounds, will be of high interest from the fundamental physics’ point of view within the ferroelectric Rashba semiconductors, FERSC [15] field. The later recently demonstrated in another W-based compound, Bi$_2$WO$_6$ [16] by some of the authors.

Here, we show by employing first-principles calculations, the study of the pressure-induced phases in the BaWO$_4$ as a function of pressure. Therefore, the dynamical stability was investigated by computing the phonon-dispersion curves. We found that, despite previous reports, the polar state in the layered phase is dynamically unstable. The latter is associated with the cancellation of octahedral rotations by the hydrostatic pressure showing; as a result, a non-polar Cmcm phase.

2. Computational Details:
In this paper, density functional calculations of the electronic and structural properties were performed using the Vienna ab-initio simulation package, vasp code [17, 18]. Projected-augmented waves, PAW [19], pseudo-potentials were used to represent the valence and core electrons. The electronic configurations for valence and semi core electrons considered in the pseudo-potentials are Ba (5$s^2$5$p^6$6$s^2$, version 06Sep2000), W (5$p^6$5$d^4$6$s^2$, version 06Sep2000), and O (2$s^2$2$p^4$, version 08Apr2002). The exchange-correlation was represented within the general-gradient approximation, GGA, in the PBEsol parametrization [20]. The periodic solution of these crystalline structures was represented by using Bloch states with a Monkhorst-Pack $k$-point mesh of (6×4×6) and 600 eV energy cut-off. These parameters were tested to give forces convergence to less than 0.0001 eV/Å and an error in total energy around ± 0.4 meV in the phases of the BaWO$_4$ compound. Additionally, the vibrational modes were fully converged with respect to energy and $k$-points mesh to obtain values in error less than 1 cm$^{-1}$. Then, full phonon-dispersion curves were computed by obtaining dynamical matrices through the DFPT [21, 22] method as implemented in vasp and later, post-processed with the Phonopy code [23].

3. Results and Discussion:
At room temperature and atmospheric pressure, the BaWO$_4$ compound crystallizes in the tetragonal scheelite within the space group $I4_1/a$ (No. 88) structure. In this structure, the W cation has an 4-fold coordination, and there is no connection between the tetrahedral sites. As

![Structure and X-Ray diffraction patterns for the BaWO$_4$ in the Cmcm, P2$_1$/c, and Cmc2$_1$ phases, respectively. The latter structures and XRD obtained at P = 30 GPa. Here, the Ba, W, and O atoms are shown in blue, grey, and red colors, respectively. The figures of the structures were elaborated with the vesta code [24] and the XRD patterns computed with the Mercury software tool [25, 26].](image)
soon as the hydrostatic pressure is applied, several phase transitions are observed experimentally. Then, a fergusonite $C2/c$ (No. 15) phase has been reported at an applied pressure close to 7.1 GPa [6]. This transformation is followed by a second phase transition at 10.9 GPa where two possible space groups were proposed: BaMnF$_4$-type ($Cmc2_1$, No. 36) structure and LaTaO$_4$-type ($P2_1/n$, No. 14) [6]. At further values of applied pressure, up to 47 GPa, the experiments only show broadening of the XRD picks suggesting the amorphization of the BaWO$_4$ compound. Interestingly, this material shows good optical, [27], electrical [9], and mechanical properties [28] in several of such phases.

At this point, theoretical studies, coupled to the experimental measurements, suggest the existence of a transition to a polar structure at $P = 10.9$ GPa and confirms its existence beyond 27 GPa [6]. Nevertheless, the confirmation of such phase is unclear due to the undefined X-ray measurements [6]. The theoretical studies from J. Lopez-Solano et al. [4, 5] were based on the Birch-Murnaghan equation of state. However, according to the reported details, non-atomic relaxation was performed under pressure, either the dynamic stability was studied.

In Fig. 1 are presented the considered layered structures that could be synthesized as a result of the applied hydrostatic pressure. In all of them, the WO$_6$ octahedral layers, in the $xz$-plane, are separated by the Ba-sites along $y$-axis. In the $Cmcm$ phase, no octahedral rotations are contained by symmetry, and the Tungsten centered octahedra is symmetrically centered in the $y$-axis (see Fig. 1). The $P2_1/c$ phase is similar to the $Cmcm$ symmetry; however, anti polar displacements of the Tungsten sites are considered along the $z$-axis. Lastly, the $Cmc2_1$ shows a similar layered structure however, octahedral rotations on top of polar Barium eigendisplacements comprise the structure. It is important to mention that all of the phases presented in Fig. 1 where fully relaxed at $P = 30$ GPa.

Also in Fig. 1 are also presented the simulated X-ray diffraction, XRD, patterns obtained with the Mercury code [25, 26] with $K_a$: Cu. These XRD patterns are presented with the aim to help the experimentalist in the possible identification of the layered phases at high pressure. Interestingly, even though the XRD are quite similar, the main differences due to the octahedral rotations and the anti polar W’s displacements are mainly condensed between $40^\circ$ to $50^\circ$ $2\theta$ values.

In Fig. 2 are presented the computed phonon-dispersion curves along the high-symmetry points in the Brillouin zone. Here, the unstable phonons (i.e. $i\omega$) are shown at negative frequency values by notation. These phonon-dispersions were obtained for the $Cmcm$ phase at 0, 12, and 30 GPa, respectively. At first glance, it can be observed that at 0 GPa the phonons related to the $Cmcm$ shows several negative branches, close to $i\omega = 200$ cm$^{-1}$. These unstable modes are associated with the instability of a such phase in the absence of hydrostatic pressure as expected from the theoretical and experimental results that confirm the scheelite $I4_1/a$ structure. In the phonon-dispersion computed for the fully relaxed $Cmcm$ structure at 12 GPa, there is an evident reduction of the negative frequencies, now around $i\omega = 100$ cm$^{-1}$, suggesting a stabilization of the layered phase. Nonetheless, this results claim for the instability of the $Cmcm$ phase at 12 GPa. In order to shed light into the debate around the BaMnF$_4$- and LaTaO$_4$-type of structures above 10.9GPa; we performed a structural relaxation of the BaWO$_4$ into these symmetries under the following methodology: First, the volume was fully relaxed by applying 12 GPa of hydrostatic external pressure. Second, in the resulting structure, only the internal atomic coordinates were allowed to relax. Third, the internal coordinates, volume, and shape were allowed to fully relax under the applied pressure. After the first step, we observed that the lowest energy structure is the $P2_1/n$ ($\Delta E_1 = E_{P2_1/n} - E_{Cmcm} = -635$ meV and $\Delta E_2 = E_{Cmc2_1} - E_{Cmcm} = 20$ meV), suggesting this phase as a ground state. Surprisingly, when the second and third steps are carried out, the WO$_6$ octahedral rotations in the $Cmc2_1$ and the anti polar Tungsten’s displacements in the $P2_1/n$ phase are entirely reduced. Then, both of the phases are converging to the layered $Cmcm$ structure.
Figure 2. (Color online) Phonon-dispersion curves for 0, 12, and 30 GPa, respectively. The latter, computed for the fully-relaxed $Cmcm$ phase of the BaWO$_4$ compound. As observed, the $Cmcm$ becomes dynamically stable after an applied hydrostatic pressure of 30 GPa. Here, the unstable phonons related to $i\omega$ frequencies are shown at negative values by notation.

Finally, at 30 GPa, a complete stable structure is observed, as suggested by the non-negative phonon-branches in the dispersion curves. The latter, confirming the stabilization, by hydrostatic pressure of the $Cmcm$ phase over the $Cmc2_1$, which was theoretically claimed as the ground state. Then, our results suggest that the applied hydrostatic pressure destroys the octahedral rotations giving; as a result, an undistorted $Cmcm$ structure. We believe that the source of the disagreement is based on the optimization process, this because in the paper by D. Errandonea et al. [6] only the volume was relaxed in order to obtain the total energy values versus the volume to be fitter by the Birch-Murnaghan equation. Unfortunately, the latter process is probably under-appreciating the effect of the hydrostatic pressure in the octahedral distortions. We hope that our results and investigation will help experimentalist and theoreticians to identify the appearance of layered structures, induced by applied hydrostatic pressure, in the ABX$_4$ compounds.

4. Conclusions:
We theoretically studied, employing first-principles calculations based on the density-functional theory formalism, the structural and vibrational properties of the BaWO$_4$ at high-pressure. We found that, although some reports claims for the existence of the polar BaMnF$_4$-type structure in the BaWO$_4$, such phase is dynamically unstable. The latter explained in terms of the cancellation of WO$_6$ octahedral rotations eigendisplacements as a function of the applied hydrostatic pressure. Therefore, the Ba polar displacements are cancelled out and the structure lies in the $Cmcm$ centrosymmetric space group.

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