High-pressure phase diagram of $BaBiO_3$

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Introduction

- Oxide perovskites exhibit a rich variety of physical properties. In this work we will investigate the structural and electronic properties of $BaBiO_3$ under pressure. This compound is an oxide perovskite which in its undoped ambient pressure phase is a charge-order insulator [1] and undergoes insulator to superconductor transition upon hole doping [2, 3]; the high pressure behavior is however unknown.
- In order to construct realistic structural models at a given pressure we use two different approaches: evolutionary algorithm for crystal structure prediction as implemented in USPEX [4] and group-subgroup analysis as implemented in the ISOTROPY software [5]. As a result high-pressure phase diagram of $BaBiO_3$ is constructed.

Structure at ambient pressure

- At low temperatures $BaBiO_3$ is monoclinic (C2/m) (later referred as *Ordinary*, Fig. 2) and undergoes two structural phase transitions: from monoclinic to rhombohedral (425 K) and than from rhombohedral to cubic (923 K). In this work ordinary structure is an object of interest and can be constructed from parent ideal cubic (Pm-3m) perovskite structure where bismuths neighboring oxygens form an octahedra (see Fig. 1) by introducing breathing (octahedras alternate its size) and tilting (octahedras are rotated) distortions.
- This structure is also characterized by a charge disproportionation of mixed-valence Bi atoms where half of all Bi atoms are Bi^{3+} atoms and half are Bi^{5+} atoms. Periodic arrangement of Bi^{3+} and Bi^{5+} forms charge density wave (CDW) state which is formed by alternating breathing-in and breathing-out distortions of oxygen octahedra.
- Under hole doping Ordinary structure undergoes insulator to superconductor transition (Fig. 3).
- A methodological way to check if our DFT description is correct by using phonon mode analysis and ISOTROPY group theory approach. We find that the $R1+$ and $R4+$ modes are unstable and they are breathing and tilting distortions respectively.
- Extending this analysis to a given pressure one can follow phonon modes evolution and find an indication of other structural phase transitions (Fig. 4).
- To get quantitatively right magnitude of breathing distortion and right value of bandgap (to find out if structure is metal or insulator) one needs to use hybrid HF/DFT calculation method.

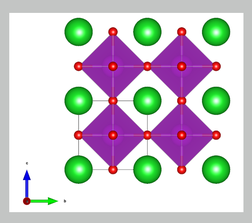


Figure 1: Cubic perovskite $BaBiO_3$.

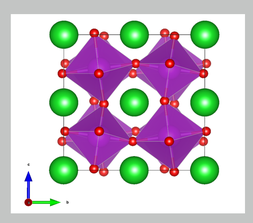


Figure 2: Monoclinic $BaBiO_3$ structure.

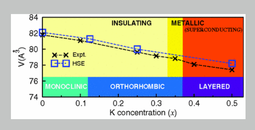


Figure 3: $BaBiO_3$ hole-doped phase diagram.

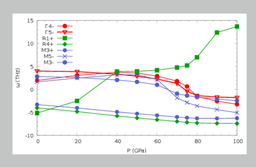


Figure 4: Perovskite $BaBiO_3$ unstable modes evolution w.r.t pressure..

Methods

For total energies and structure optimization:

- DFT calculations using GGA and HSE functionals as implemented in VASP.
- Phonopy for phonon calculations to test the stability of structures.

To construct realistic structural models we employ two approaches:

- ISOTROPY[5]. Based on the phonon analysis of the parent cubic phase made using *Phonopy* three unstable modes were found: $M3+$, $R1+$ and $R4+$. ISOTROPY offers a way to combine this modes and generate accordingly distorted structures. The method is described in [6]. Advantage: powerful tool based on group theory and gives meaningful resulting structures. Disadvantage: distortion should obey symmetry relations proposed by one of the parent subgroups so one can get only structures that are modification of parent perovskite (i.e. no amorphous, layered structures etc.).
- USPEX[4]: evolutionary algorithm for crystal structure prediction. The main idea of this method is to start from pool of random structures and evolve them to right one by mutating lattice parameters and atoms position and by creating new structures from combination of old ones. This leads to very broad structural search in phase space.
- "By hand". Two interesting structures: layered (Fig. 5) and post-perovskite (Fig. 6) [7] where added into our pool of structures manually.

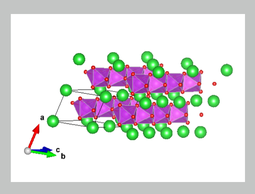


Figure 5: Layered perovskite $BaBiO_3$ structure.

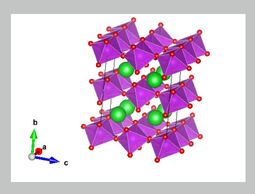


Figure 6: Post-perovskite $BaBiO_3$ structure.

Structural and electronic properties of the Ordinary (low-T experimental) structure

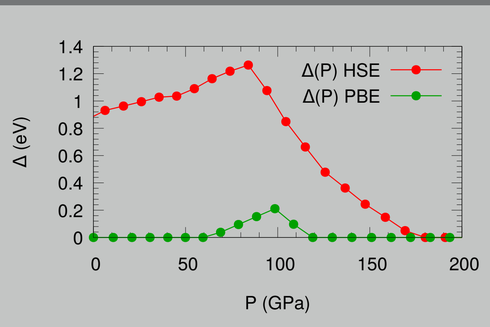


Figure 7: Bandgap Δ evolution w.r.t pressure.

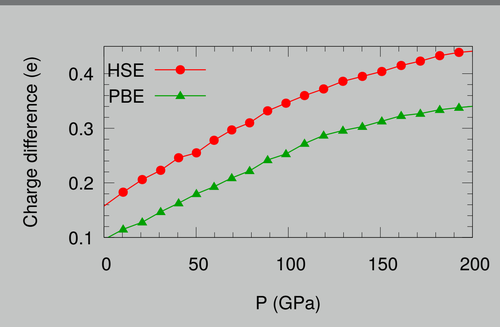


Figure 8: Bi^{5+} and Bi^{3+} charge difference evolution w.r.t pressure.

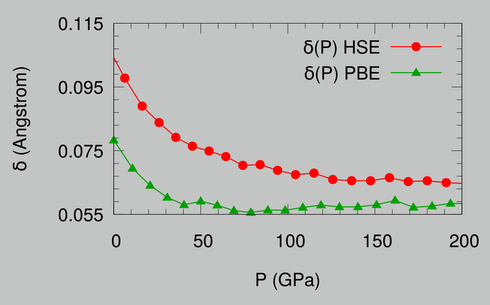


Figure 9: Breathing δ distortions w.r.t pressure.

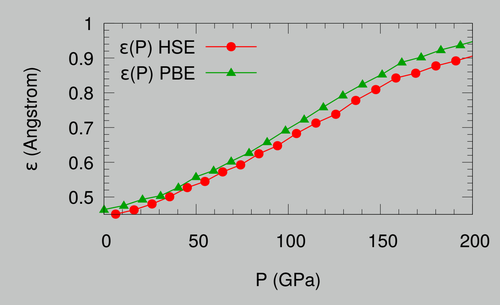
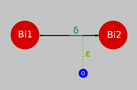


Figure 10: Tilting ε distortions w.r.t pressure.



Structural and electronic properties of the Ordinary (low-T experimental) structure

- Although the value of the breathing distortion ε is underestimated, PBE is still able to describe structures qualitatively and can be used for structural search. But in order to get the right quantitative bandgap Δ estimation one needs to use HSE.
- At ambient pressure the Ordinary $BaBiO_3$ structure is insulating with an indirect bandgap of ~ 1.0 *eV* (exp 1.1 eV)[3] and undergoes an insulator to metal transition at about 180 GPa (Fig. 7).
- CDW is not suppressed under pressure (see Fig. 8). Structural breathing δ and tilting ε distortions are still present (see Fig. 15 and Fig. 16).

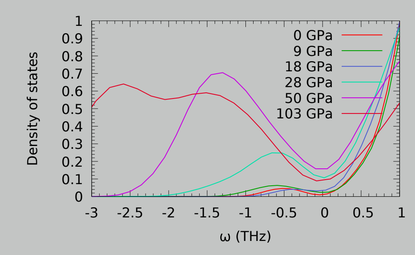


Figure 11: $BaBiO_3$ Ordinary structure phonon DOS.

The ordinary $BaBiO_3$ structure becomes dynamically unstable for pressures higher than about 28 GPa (Fig. 11). This is why one needs to do a structural search to find energetically favorable and dynamically stable structures at high pressure.

High-pressure phase diagram

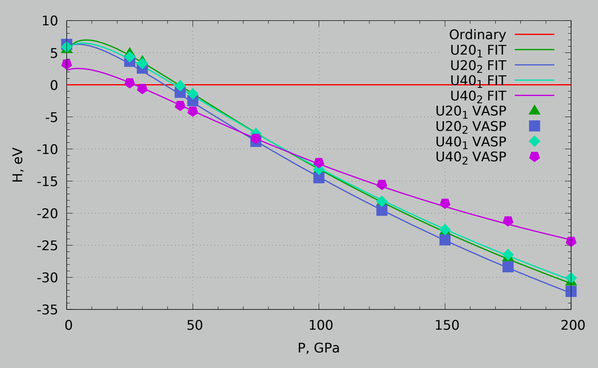


Figure 12: High-pressure phase diagram of $BaBiO_3$.

Due to computational reasons we were restricted to analyze only 10, 20 and 40 atoms structures. Using USPEX structures where generated at 50 GPa and 100 GPa pressures and ISOTROPY structures were generated using eigenvector analysis of the perfect cubic structure at 100 GPa. Later all structures where optimized for the given pressure using VASP for structural relaxation keeping volume of the cell fixed to the given value. Four the best structures from our pool of structures are presented here. We find two structural phase transitions: at about 27 GPa from Ordinary structure to 40 atoms cell $U40_2$ structure and from $U40_2$ to $U20_2$ at about 70 GPa.

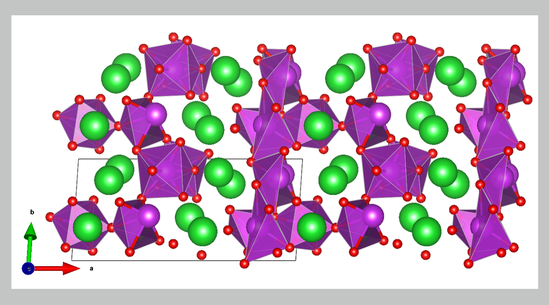


Figure 13: $BaBiO_3$ $U40_1$ structure.

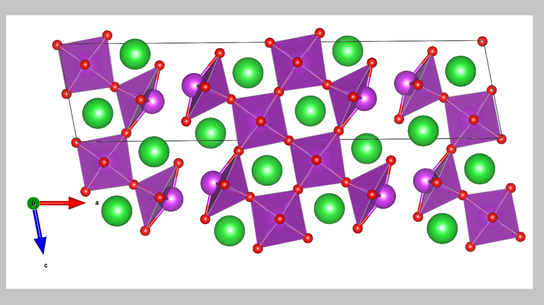


Figure 14: $BaBiO_3$ $U40_2$ structure. Stable between ~ 27 *GPa* and ~ 70 *GPa*.

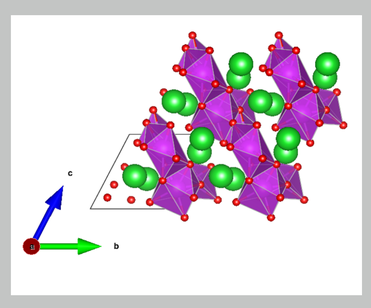


Figure 15: $BaBiO_3$ $U20_1$ structure.

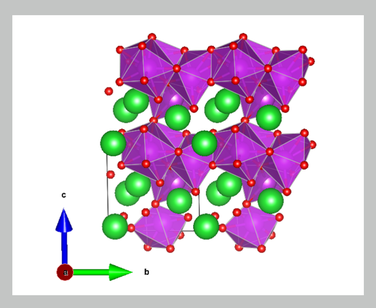


Figure 16: $BaBiO_3$ $U20_2$ structure. Stable starting from ~ 70 *GPa*.

Conclusions

- For the Ordinary structure the CDW state is not suppressed and the structural distortions are still present under pressure. We find an insulator to metal transition at about 180 GPa. however the structure becomes dynamically unstable at about 28 GPa and this indicates that a structural search is needed.
- "Work in progress": using USPEX and ISOTROPY structural search we generate a pool of candidate structures at high pressure. Our preliminary calculations show two structural phase transitions at 27 GPa and 70 GPa. The corresponding structures contain 40 and 20 atoms in the unit cell respectively. These structures are highly distorted and cannot be obtained as simple distortions of the parent perovskite structure.
- "TODO:" analyze electronic properties of the obtained structures and refine the phase diagram.

References

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Acknowledgments

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