# High-pressure phase diagram of $BaBiO_3$

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## Abstract

$BaBiO_3$ is a well-known example of a 3D *charge density wave* (CDW) compound, in which the CDW behavior is induced by charge disproportionation at the Bi site. At ambient pressure, this compound is a charge-ordered insulator, but little is known about its high-pressure behavior. In this work, we study from first-principles the high-pressure phase diagram of $BaBiO_3$ using phonon modes analysis and evolutionary crystal structure prediction. We show that charge disproportionation is very robust in this compound and persists up to 100 GPa. This causes the system to remain insulating up to the highest pressure we studied.

## Motivation

- 3D charge density wave (CDW) at ambient pressure due to *breathing* and *tilting* distortions of the perovskite structure and $Bi^{3+}/Bi^{5+}$ charge disproportionation.
- Undoped $BaBiO_3$ is an insulator due to CDW and hole doping suppress CDW and induces superconductivity [1, 2, 3] (Fig. 1).

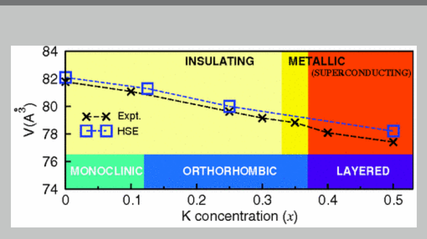



Figure 1: $BaBiO_3$ hole-doped phase diagram.

- Can we induce SC with pressure? (as in transition metal chalcogenides [4, 5])

## Methods

- DFT calculations using GGA and HSE functionals as implemented in `VASP`.
- Phonopy [6] for phonon calculations.
- Evolutionary prediction (EP) algorithm for crystal structural prediction using `USPEX` package [7].
- Group-theoretical symmetry analysis (SA) using `ISOTROPY` software suite [8].

## Structures and phase diagram

- $BaBiO_3$ undergoes three structural phase transitions (monoclinic $\rightarrow$ (20 GPa) $\rightarrow$ triclinic $\rightarrow$ (28 GPa) $\rightarrow$ "clustered" $\rightarrow$ (87 GPa) $\rightarrow$ distorted) and remains insulating up to 100 GPa.
- Structures obtained using evolutionary prediction algorithms (EP) are systematically lower in energy than structures obtained with symmetry analysis (SA) algorithm.

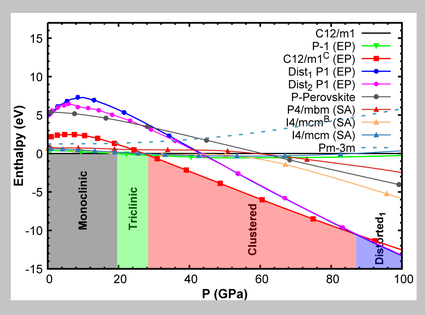



Figure 2: Predicted high-pressure phase diagram of $BaBiO_3$. (EP) means that structures were obtained using the evolutionary algorithms structure prediction method (Evolutionary Prediction) and (SA) – using group-theoretical approach (Symmetry Analysis)

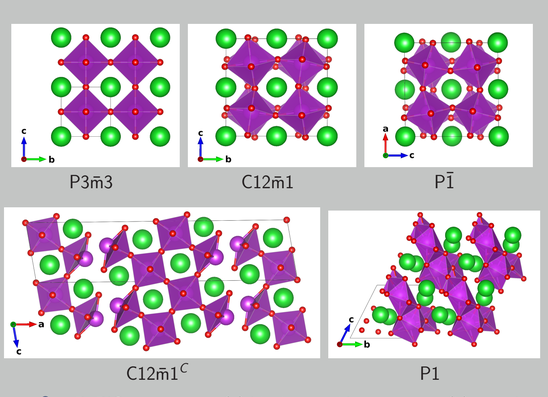



Figure 3: $BaBiO_3$ structures: (a) ideal perovskite structure; (b) experimental $BaBiO_3$ structure for ambient pressure; (c) triclinic structure; (d) *"clustered"* monoclinic structure; (e) non-symmetric "distorted$_1$" structure. Big green spheres are Ba atoms, big violet spheres are Bi atoms and small red spheres are O atoms.

## Electronic properties of ground state structures

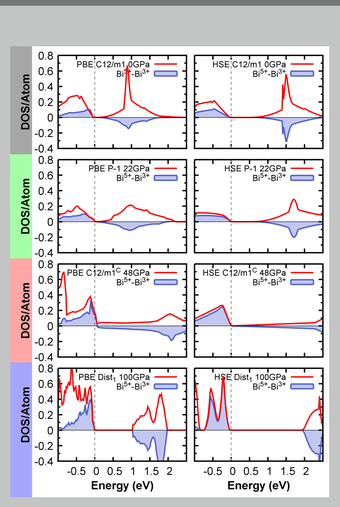



Figure 4: DOS/atom and the difference of average PDOS for $Bi^{5+}$ and $Bi^{3+}$ atoms.

- We calculated electronic properties of all ground state structures using PBE and HSE functionals.
- The use of HSE is essential as PBE severely underestimates the band gap.
- All four ground-state structures are insulating at HSE level (Fig. 4).
- All the structures have two inequivalent Bi atoms with different "formal" valence states.
- The insulating behavior is associated with the charge disproportionation.

## Symmetry analysis

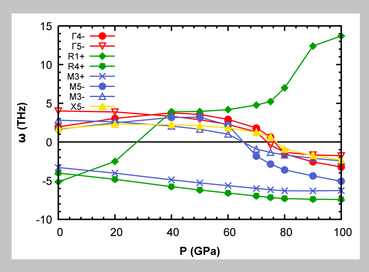


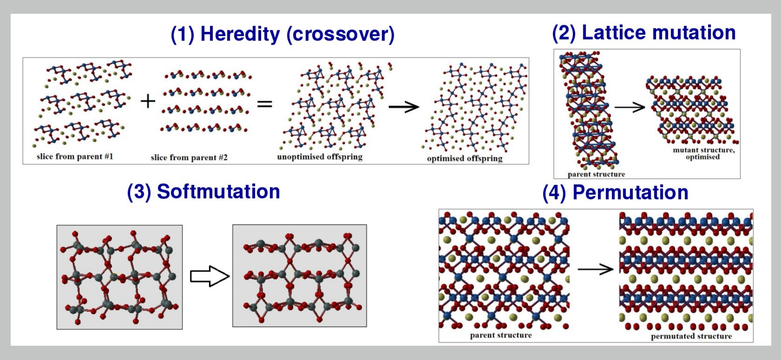

Figure 5: Perovskite $BaBiO_3$ unstable modes evolution.

| Irreps | Order parameter | Space group | | Atoms |
|---|---|---|---|---|
| M3+M5- | (0;0;a\|0,0;0,0;b,0) | Amm2 | 38 | 20 |
| M3+M5- | (0;0;a\|0,0;0,0;b,b) | Pmc2_1 | 26 | 10 |
| M3+R4+ | (0;a;-a\|a,0,0) | P4_2/nmc | 137 | 40 |
| M3+R4+ | (a;0;0\|b,0,0) | P4/mbm | 127 | 20 |
| M3+R4+ | (0;a;-a\|0,0;0,b;-b,0) | I-4m2 | 119 | 40 |
| M3+R4+ | (0;a;0\|a,a,0) | Pnma | 62 | 20 |
| M3+R4+ | (a;b;c\|a,0,0) | Pmmn | 59 | 40 |
| M5-R4+ | (0,0;0,a;-a,0\|b,0,0) | P4_2/nmc | 131 | 40 |
| M5-R4+ | (0,0;a,0;0,a\|b,0,0) | P4/nnc | 126 | 40 |
| M5-R4+ | (a,0;0,0;0,0\|b,b,0) | Cccm | 66 | 40 |
| M5-R4+ | (0,a;0,0;0,0\|b,b,0) | Cmmm | 65 | 40 |
| M5-R4+ | (a,0;0,0;0,0\|b,0,0) | Cmcm | 63 | 40 |
| M5-R4+ | (a,0;0,0;0,b\|c,0,0) | Pnnm | 58 | 40 |
| M5-R4+ | (a,a;0,0;0,0\|b,0,0) | Pbcm | 57 | 20 |
| M5-R4+ | (0,0;0,a;0,b\|c,0,0) | Pmna | 53 | 40 |
| M5-R4+ | (0,0;a,0;b,0\|0,0,c) | Pnna | 52 | 40 |
| M5-R4+ | (a,0;0,0;0,0\|0,b,0) | Pmma | 51 | 40 |

- Symmetry analysis is commonly used to investigate the perovskite compounds [9, 10].
- The ideal cubic perovskite $BaBiO_3$ is dynamically unstable at ambient pressure and room temperature.
- The stable structure can be obtained following the most favorable distortion, which may be a linear combination of unstable phonon eigenvectors.
- Modes that are unstable at 100 GPa were combined to predict high-pressure $BaBiO_3$ structures [11].
- 17 structures were constructed with 10, 20 and 40 atoms in the unit cell (Table 1).

## Ab-initio evolutionary prediction

- Evolutionary prediction algorithm is an unbiased method for crystal structure prediction.
- Idea: start from a pool of random structures and evolve them by mutating lattice parameters and atoms position and by creating new structures from combination of old ones.




- We generated structures with 10, 20 and 40 atoms in the unit cell at 50 and 100 GPa (EP in Fig. 2).
- The obtained structures are systematically lower in energy than SA structures.

## Neighbors analysis

- Our calculations show that $BaBiO_3$ has a tendency to become more distorted when pressure is increased.
- In order to quantify this tendency we have performed an analysis of the coordination environment of Bi using the `CHEMENV` package [12].
- The coordination environment of a specific atom is determined probing all possible meaningful model polyhedra in order to find the one which is the most similar to the local environment without non-relevant neighbors which are defined by cutoff in the distance or/and angle.
- Our analysis shows that number of Bi neighbors increases when pressure is increased deviating from the octahedral environment.

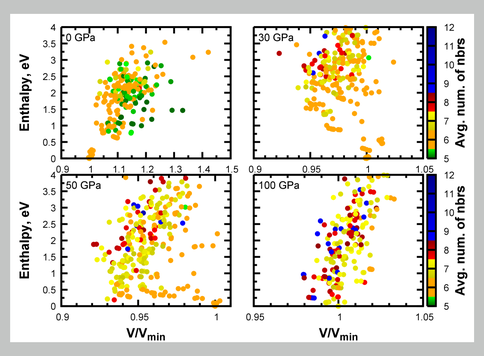



Figure 6: Average number of O neighbors of Bi atoms for a pool of two f.u. $BaBiO_3$ structures obtained using the evolutionary algorithms approach. Each dot is associated with a specific structure and its color denote the average number of neighbors. The pool of structures consists of around 300 structures for each pressure with 10 atoms in the unit cell.

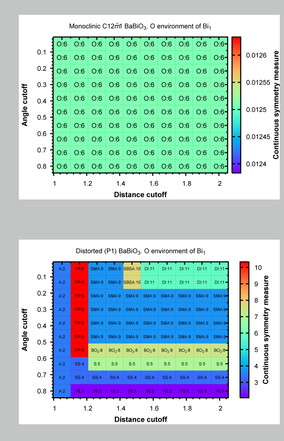



Figure 7: Environment analysis for monoclinic (C12̃m1) and distorted (P1) $BaBiO_3$.

## Conclusions

- We investigated the possibility of suppression of the CDW at high pressure which could lead to insulator to metal transition in $BaBiO_3$ compound.
- We used two different structural search approaches to construct the high-pressure phase diagram of the $BaBiO_3$: evolutionary algorithms and phonon mode analysis.
- The resulting phase diagram shows three structural phase transitions.
- The group-theoretical structural prediction method alone is not able to find the best structures at high pressure as it is constrained only to structures with perovskite symmetry.
- Using evolutionary algorithms we found that $BaBiO_3$ becomes more distorted with increasing pressure.
- All ground-state structures remain insulating up to 100 GPa and the charge disproportionation is preserved at high pressure.

## References

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[12] `chemenv` is a module inside `pymatgen` package and is developed by David Waroquiers and Geoffroy Hautier. Website: `http://pymatgen.org/`.

Ab-initio prediction of the high-pressure phase diagram of $BaBiO_3$
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`http://arxiv.org/abs/1702.04600`

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