Ab-initio study of ABiO$_3$ (A=Ba, Sr, Ca) under high pressure

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Using ab-initio crystal structure prediction we study the high-pressure phase diagram of ABiO$_3$ bismuthates (A=Ba, Sr, Ca) in a pressure range up to 100 GPa. All compounds show a transition from the low-pressure perovskite structure to highly distorted, low-symmetry phases at high pressures (PD transition), and remain charge disproportionated and insulating up to the highest pressure studied. The PD transition at high pressures in bismuthates can be understood as a combined effect of steric arguments and of the strong tendency of bismuth to charge-disproportionation. In fact, distorted structures permit to achieve a very efficient atomic packing, and at the same time, to have Bi-O bonds of different lengths. The shift of the PD transition to higher pressures with increasing cation size within the ABiO$_3$ series can be explained in terms of chemical pressure.

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I. INTRODUCTION

The study of the competition between superconductivity and charge ordering phenomena has received a strong impulse from recent experiments on high-$T_c$ cuprates and transition metal dichalcogenides, raising questions on their interplay and, more in general, on the role of critical fluctuations in quasi-two-dimensional systems.

However, the competition between superconductivity and charge density wave (CDW) ordering is not limited to two-dimensional systems, but has been observed in other systems with different dimensionality. A classical example is that of bismuthates with chemical formula ABiO$_3$, where A is an alkaline earth (Ba, Sr, or Ca). These compounds are charge-ordered insulators, but undergo an insulator-to-metal transition upon doping, reaching superconducting $T_c$’s as high as 34 K.

The CDW is associated to the mixed-valence behavior of bismuth, which can acquire two formal oxidation states – Bi$_{3}^{+}$ and Bi$_{5}^{3+}$ – which alternate on a perovskite lattice, giving rise to tilting and breathing distortions. The charge difference is significantly lower than 2e$^-$ due to the strong hybridization between Bi(s) and O(p) states. Based on this consideration an alternative picture has been proposed invoking the condensation of holes in low-est O band, resulting in the formation of Bi$_{5}^{3+}$L$_{2}^{-}$ + Bi$_{3}^{+}$, where L identifies the ligand hole. These two pictures are not mutually exclusive and it is likely that both processes (charge ordering and ligand hole) contributes to the opening of the CDW gap. Upon doping, the distortion is gradually suppressed and the lattice returns to the ideal perovskite structure, which is metallic and superconducting.

Naively, one would expect that extreme pressures could be used to suppress the lattice distortion also in the undoped samples, and hence achieve a metallic, possibly superconducting state without the complications introduced by doping. However, as shown in our previous work on BaBiO$_{3}$ and independently confirmed by a combined theoretical and experimental work, high pressures do not stabilize an ideal perovskite structure, but a strongly distorted, amorphous-like structure, characterized by strong charge disorder and insulating behavior.

![Figure 1](color online) Phase diagram of the structural phase transitions in ABiO$_3$ compounds. Each transition is labeled by a symbol which represents the rank of the structure in the sequence of transitions: filled circle for Structure I, square for Structure II, diamond for Structure III and pentagon for Structure IV. “Dark-gray” (“blue”) region contains perovskite-like (P) structures, “light-gray” (“red”) – distorted (D) structures and “stroked” (“green”) non-perovskite (NP) structures. The thick dashed line indicates the transition line for the perovskite-to-distorted transition (PD transition) estimated from chemical pressure considerations, as explained in Section II.

In this work, we investigate this phenomenon further, and address the effect of chemical pressure, studying the high-pressure phase diagram of the whole family of ABiO$_3$ compounds.
ABiO$_3$ compounds (A=Ca, Sr, Ba) with methods for evolutionary ab-initio crystal structure prediction.

The electronic spectra of all predicted phases are computed with hybrid Hartree-Fock/density functional theory (DFT) functional with the HSE (Heyd-Scuseria-Ernzerhof) exchange-correlation functional which has been demonstrated to accurately describe the CDW insulating state of BaBiO$_3$, while ordinary DFT describes BaBiO$_3$ as a metal.

Our results show that the ordered CDW at low pressures and the increase charge disproportionation at high pressure, accompanied by larger structural distortions, are general features of the bismuthate phase diagram: in fact, as shown in Fig. 1, all compounds undergo a transition from a perovskite (P) to a strongly distorted (D) structure, and remain insulating up to 100 GPa. The occurrence of distorted structures is a consequence of a steric argument, combined with the tendency of bismuth to charge disproportionation.

This paper is organized as follows: in Section II we describe the results of our ab-initio calculations starting with our prediction for the high-pressure phase diagram in Subsection II.A followed by the description of electronic properties of the most stable structures in Subsection II.B. The discussion on the perovskite-distorted transition (PD transition) follows in Section III. The main conclusions of this work are summarized in Section IV. Computational details are described at the end of the paper in Section V.

II. RESULTS

A. Phase Diagram

In Fig. 1 we show the phase diagram of ABiO$_3$ in the pressure range from 0 to 100 GPa, predicted using ab-initio evolutionary crystal structure prediction methods. For Bismuthates, the use of an unbiased crystal structure prediction method is crucial, since the group-subgroup approach which is routinely used to predict structural transitions in perovskites is not able to capture the transition to the distorted structure – see Ref. [12] for details.

To generate the phase diagram in Fig. 1, a set of reference crystal structures were first obtained from evolutionary crystal structure prediction runs at 0, 50 and 100 GPa. The most promising structures from the pool of crystal structures obtained at these pressures are further relaxed at intermediate pressures at constant volume intervals, and interpolated with an analytical equation of state, which allowed us to determine the transition pressures accurately (see Sec. V for more details). The lowest-enthalpy structures at each pressure were then used to construct the final phase diagram.

We have plotted all ABiO$_3$ compounds on the same figure (Fig. 1), with a common pressure axis; the compounds are equispaced along the vertical axis; starting with Ca, which has the smallest ionic radius, the size of the A cation increases along the y axis from Ca to Ba exerting an effective chemical pressure on the perovskite lattice (see Table I for corresponding ionic radii and unit cell volumes). Assuming that the most important parameter governing the structural transitions is the volume of the unit cell, and that this is mainly determined by the size of the A cation, this means that the sequence of structural transitions seen in BaBiO$_3$ should occur at lower pressures in SrBiO$_3$ and even lower in CaBiO$_3$.

In the figure, each transition is labeled by a symbol representing the rank of the structure in the transition series. The diagram is also divided into three regions, denoted with the letters P (perovskites), D (distorted) and NP (non-perovskite). The thick dashed line indicates the shift of perovskite-to-distorted transition pressure (PD transition), estimated from the simple cubic perovskite model, as explained in Section III.

We start from the low-pressure region. An empirical guess of the ambient pressure structure for each compound can be obtained from the Goldschmidt tolerance factor, which is based on the size mismatch between the cations. The tolerance factor for double perovskites is defined as: $t = \frac{r_A + r_O}{\sqrt{2(r_B^+ + r_O)}}$, where $r_A$ is the radius of the A cation, $r_{Bi}^+$ is averaged ionic radius of bismuth and $r_O$ is radius of oxygen. The ideal value $t = 1$ corresponds to a cubic perovskite structure; deviations from this ideal value indicate the amount of distortion needed to stabilize the atomic arrangement: the higher the deviation, the higher the distortion. Based on the value of $t$, one would expect that at ambient pressure all ABiO$_3$ compounds should be either monoclinic or orthorhombic perovskites with tilted oxygen octahedra, because $t < 0.92$ for all A cations (see Table I). Indeed, the tolerance factor correctly predicts the structure at ambient pressure for BaBiO$_3$ and SrBiO$_3$, which are known experimentally. However, the structure obtained by our evolutionary algorithm predictions for CaBiO$_3$ is trigonal, which apparently contradicts the argument based on the tolerance factor. Note, however, that in this case the value of $t$ is extremely small, and several exceptions to the tolerance factor argument are known.

At ambient pressure BaBiO$_3$ and SrBiO$_3$ structures exhibit different monoclinic symmetries: C12/m1 and P2$_1$/c respectively (see Fig. 2c and 2d). Both structures contain the characteristic perovskite building block formed by BiO$_6$ octahedra and share a common parent structure – an ideal cubic perovskite with P3m1 symmetry. The two monoclinic structures can be obtained applying two different types of distortions to the parent structure: breathing (alternating the size of Bi-O octahedral environment) and tilting (rigid rotations of Bi-O octahedra). The difference between the two compounds is the different tilting pattern ($a^0b^-b^-$ and $a^+b^-b^-$ for BaBiO$_3$ and SrBiO$_3$ in Glazer notation respectively) and the amount of breathing distortion (0.074 Å and 0.089 Å, see Table I).
Table I. Ion Shannon radii (R) for the A cation in coordination XII; corresponding tolerance factors (t) for A\textsubscript{BiO\textsubscript{3}} compounds in the double perovskite structure; calculated volume per formula unit (V), average Bi-O distance (Bi\textsubscript{O}) and breathing distortion δ for A\textsubscript{BiO\textsubscript{3}} at P=0 GPa. δ = 1/4(Bi\textsubscript{1O} − Bi\textsubscript{2O}), where Bi\textsubscript{1O} and Bi\textsubscript{2O} are average Bi\textsubscript{1}−O and Bi\textsubscript{2}−O bond distances respectively.

| Compound   | R(A) (Å) | V (Å\textsuperscript{3}/f.u.) | t | Bi\textsubscript{O} (Å) | δ (Å) |
|------------|----------|-------------------------------|---|------------------------|-------|
| CaBiO\textsubscript{3} | 1.34     | 76.91                         | 0.85 | 2.29 | 0.122 |
| SrBiO\textsubscript{3} | 1.44     | 80.00                         | 0.88 | 2.25 | 0.089 |
| BaBiO\textsubscript{3} | 1.61     | 85.87                         | 0.93 | 2.24 | 0.074 |

Upon increasing pressure we observe that all compounds undergo a series of structural transitions. The common feature is that all A\textsubscript{BiO\textsubscript{3}} compounds undergo a transition to a highly distorted phase (D) beyond some critical pressure. By highly distorted phase we mean a structure that does not belong to the perovskite family, in the sense that a transition from the perovskite structure requires large atomic displacements and strong distortions of the original structural motifs, which cannot be decomposed into breathing and tilting distortions\textsuperscript{25}. Even though they do not exhibit the regular arrangement seen at ambient pressures, the Bi sites in the high-pressure distorted structures exhibit charge disproportionation and insulating behavior, as discussed in Sect. IIB.

Distorted structures in the bismuthates were predicted for the first time by us in BaBiO\textsubscript{3}\textsuperscript{12}, and later confirmed by Ref. \textsuperscript{13}.

We now describe the phase diagrams of the individual compounds in detail; the corresponding structural files are provided in Supplementary Materials.

**BaBiO\textsubscript{3}**: The data for BaBiO\textsubscript{3} presented in this work are taken from our previous work\textsuperscript{12}. We find that a first transition from the monoclinic I(P) (space group C12\textsubscript{1}n1; see Fig. 2a) to triclinic II\textsubscript{(P)} structure occurs at 20 GPa. The II\textsubscript{(P)} structure is another form of perovskite structure with an additional octahedral tilting axis compared to the I(P) structure. The next transition is from the triclinic II\textsubscript{(P)} to a clustered monoclinic III\textsubscript{(P)} structure at about 28 GPa. This structure can be described as a perovskite with the stacking fault resulting in only half of the Bi atoms exhibiting an octahedral environment. Although it strongly deviates from the perovskite structure, we still assign it to the perovskite family (P). The last transition is from a clustered monoclinic to a distorted IV\textsubscript{(D)} (see Fig. 2f) structure at 87 GPa, which has no symmetry.

**SrBiO\textsubscript{3}**: The first transition is from a perovskite-like monoclinic I\textsubscript{(P)} (space group P12\textsubscript{1}n1; see Fig. 2b) to a distorted II\textsubscript{(D)} structure at about 25 GPa (see Fig. 2c) and the second is from a distorted II\textsubscript{(D)} to another distorted structure III\textsubscript{(D)} at 65 GPa. These are two different distorted structures, but is difficult to give a clear description of the structural differences as the structures are too distorted to identify a clear pattern.

**CaBiO\textsubscript{3}**: There are no experimental crystal structure data for CaBiO\textsubscript{3} at ambient pressure, but only a computational study suggesting a polar R3 structure\textsuperscript{23}. Indeed, CaBiO\textsubscript{3} is unstable at ambient conditions but it is possible to stabilize it at high pressures\textsuperscript{26} (about 6 GPa), or upon K doping, Ca\textsubscript{2}K\textsubscript{1−x}O\textsubscript{3}, with 0.15 ≤ x ≤ 0.2\textsuperscript{25}. According to our evolutionary predictions the structure at ambient pressure is trigonal (R3) and consists of “paired” distorted octahedra that share a common edge. We find that the Bi-Bi and Ca-Ca environment is no longer octahedral, as in perovskites, but tetrahedral. Therefore, in Fig. 1 this structure is classified as a non-perovskite structure (NP). Our structure is 12 meV/atom (17 meV/atom in HSE) lower in enthalpy than the perovskite structure proposed by He \textit{et al.} in Ref. \textsuperscript{23} and based on the traditional group-subgroup symmetry analysis\textsuperscript{20}.

The first structural transition is from the trigonal I(NP) (see Fig. 2a) to monoclinic II\textsubscript{(P)} structure at 7 GPa. In this case the Bi-Bi and Ca-Ca environment is distorted octahedral and the Bi-O octahedra are distorted too, with additional tilting. We therefore classify this structure as perovskite (P). The second transition is from the II\textsubscript{(P)} to a distorted III\textsubscript{(D)} (see Fig. 2f) structure with C1c1 symmetry at 22 GPa.

In summary, our study of the phase diagram of A\textsubscript{BiO\textsubscript{3}} compounds shows that pressure does not stabilize more symmetric structures, as in other transition metals perovskites, but highly distorted ones, as we originally observed for BaBiO\textsubscript{3}\textsuperscript{12}. Furthermore, reducing the size of the A cation shifts the transition from perovskite-like to distorted structures to a lower pressure, in agreement

![A-cation radius](image-url)
with considerations based on chemical pressure, i.e., with the idea that substituting a cation with a smaller one is equivalent to applying an external pressure. In the next sections, we will study in more detail the nature and origin of the PD transition and the electronic properties of the most relevant structures.

### B. Electronic Structure

Fig. 3 shows the total and atom-projected density of states (DOS) for all ABIO$_3$ compounds, at the transition pressure between the perovskite (P) and the distorted (D) structures, obtained with the HSE functional. For consistency, also for BaBiO$_3$ we show the DOS for the perovskite and the distorted structures, at the transition pressure between the two, but we remind that in this region the stable structure is the clustered one. The aim of the figure is in fact to trace the origin of the PD transition, which is common to all ABIO$_3$ compounds, while the clustered region is found only in BaBiO$_3$.

As it can be clearly seen, all structures are insulating, with a gap at ambient pressure: 0.6 eV for BaBiO$_3$ (experimental measurements vary from 0.2 eV to 1.1 eV), 1.1 eV for SrBiO$_3$ and 2.6 eV for CaBiO$_3$. The increase of the gap with decreasing cation size is consistent with the larger breathing distortions predicted for the CaBiO$_3$ structure (see Table 1). The behaviour of the gap as a function of pressure is shown in Fig. 3.

The mechanism leading to the opening of a gap in the perovskite structure has been discussed by several authors: charge disproportionation at the Bi site causes alternating breathing distortion of the ideal perovskite lattice, further stabilized by tilting distortion, and this opens a gap in the strongly hybridized Bi(s)-O(p) antibonding band. This is evidenced by the partial DOS plots, which show a clear splitting and charge redistribution between Bi$^{3+}$ and Bi$^{5+}$ states, localized below and above the semiconducting gap. A similar situation is found in distorted phases, where it is still possible to identify inequivalent Bi$^{3+}$ and Bi$^{5+}$– like ions. One clearly sees that the two contributions to the DOS are well separated, with Bi$^{5+}$ and Bi$^{3+}$ states giving the dominant contribution to the electronic DOS above and below the gaps, respectively. In distorted SrBiO$_3$ and BaBiO$_3$ the two main peaks are further split into several sub-peaks, indicating a more complex pattern of charge disproportionation.

In typical transition metal perovskites the application of pressure leads to a continuous closing of the gap. However, for Bismuthates the situation is different: increasing pressure by chemical substitution makes the gap larger, due to the gradual narrowing of the Bi$^{3+}$ and Bi$^{5+}$ peaks associated with the upward shift and broadening of the occupied Oxygen band. Despite the larger degree of Bi-O hybridization the narrowing of the Bi$^{3+}$ and Bi$^{5+}$ peaks increases the bonding-antibonding repulsion, increases the bond- (see Table 1) and charge-disproportionation (see Fig. 5) and ultimately lead to a substantial increase of the gap size.

As already mentioned, the classification into Bi$^{3+}$ and Bi$^{5+}$ is clearly only indicative: due to the strong hybridization with oxygen the actual charge disproportionation between Bi sites is much smaller than two. In order to obtain a quantitative estimate, we performed a Bader charge analysis, which is more accurate than the estimation based on the integration of the DOS, that we used in our previous works. Remarkably, we found that Bader charge analysis deliver charge differences between Bi$^{3+}$ and Bi$^{5+}$ ions 3-4 times larger. The results are shown in Fig. 5, where $\Delta \rho$ is a difference between the maximum and minimum charge located on bismuth atoms obtained in the Bader analysis. Each symbol in the figure represents a specific structure and its filling shows if the structure is perovskite-like – filled symbol – or distorted – empty symbol. The figure shows that the average charge difference is of $\sim 0.5$ e$^-$/f.u., and slightly increases with pressure; apart from BaBiO$_3$, where the position of the clustered structure complicates the phase diagram, the transition from the perovskite to the distorted structure is relatively smooth, similarly to what we observed for the DOS.

Having clarified the reasons behind the robustness of the CDW gap upon pressure we move now to the analysis of the PD structural transition, which is done in the following section.

### III. PEROVSKITE-TO-DISTORTED TRANSITION

The first obvious argument to explain the PD transition is a steric one, i.e., distorted structures, which are very compact, become favorable at high pressures, where the $pV$ term becomes the dominant part of the total enthalpy. In fact, at the transition pressures between perovskite and distorted structures, the volumes of the distorted structures are on average $\sim 7.5$% smaller than those of the perovskite ones.

The lower specific volume of the distorted structures is achieved by a more efficient packing of the atoms with an increasing coordination number. To visualize this, in Fig. 7 we plot the average number of oxygens in bismuth environment as a function of pressure. Values close to six represent perovskite or perovskite-like structures. The higher the difference from this value, the higher the amount of distortion in the structure.

Clearly, all ABIO$_3$ compounds undergo a discontinuous jump from perovskite-like structures to distorted ones at different critical pressures: CaBiO$_3$ and SrBiO$_3$ at 22-25 GPa; and BaBiO$_3$ at 87 GPa (45 GPa if the clustered structure is neglected). Thus, the increase of coordination number is the general mechanism that stabilizes distorted structures at extremely high pressures in agreement with what we found for BaBiO$_3$ in the previous paper.
The origin of this effect can be understood as follows: initially, pressure causes a compression of the Bi-O bonds. However, the compressibility of Bi-O bonds decreases with increasing pressure, until it reaches a critical value, where it becomes energetically more favorable to introduce new chemical bonds and rearrange bond distances than to continue to compress bonds.

This can be easily seen from Figure 7, showing the pressure-dependence of the average Bi-O length; for all ABIO3 compounds there is a clear jump to larger Bi-O length at the pressures corresponding to the transition from perovskite-like to distorted structure. The increase in coordination number, and the tendency to form disordered structures, is also favored by the intrinsic tendency of bismuth to charge disproportionation, which leads to forming two (or even more) types of bonds with different lengths. The tendency to charge disproportionation increases with increasing pressure, as shown by the Bader charge analysis in Fig. 5, and hence the arrangement in high-symmetry structures becomes progressively less favorable.

Indeed, forming distorted structures, which have a very low symmetry, is an efficient way to increase the number of bonds in a very closely-packed structure. Let us consider first the Bi-O octahedral environment: the Bi-O coordination geometry is restricted by the chemical composition and crystallographic restriction theorem, which forbids Bi-O to form a regular polyhedron with coordination number larger than six. For example, the 7-coordinated pentagonal dipyramid has a 5-fold rotational symmetry and the 8-coordinated square antiprism has an 8-fold symmetry, which are both forbidden due to the crystal periodicity. Cubic coordination is not allowed by chemical composition as it requires a composition with the same number of Bi and O. As a result, when the coordination number increases due to the formation of new bonds under increasing pressure, pronounced distortions of the local environment occur, that lead to highly-distorted structures at high pressure.

The perovskite-to-distorted transition pressure increases with increasing cation radius (see Fig. 1). This effect, sometimes referred to as chemical pressure, is based on the idea that replacing a cation with a larger one, keeping the volume fixed, increases the effective pressure on the BiO3 sublattice. This effect is easily illustrated by a simple numerical experiment, based on the ideal cubic perovskite structure.

Fig. 3 shows the equation of state (EOS) for ABIO3 compounds in cubic structure. The influence of chemical pressure may be estimated calculating the pressures, corresponding to the intersection of a $V = V_{PD}$ line with the EOS curve for a given compound. For example, according to Fig. 3, the PD transition pressure for CaBiO3 is at around 22 GPa. We can use this value and the EOS for our cubic model to estimate the PD transition pressures in SrBiO3 and BaBiO3. First, we find the volume, which corresponds to 22 GPa on the EOS for cubic CaBiO3 ($V_{PD}$). If we assume that the main driving force of the PD transition is the unit cell volume, we can estimate the PD transition pressure for SrBiO3 and BaBiO3 from the intersection of the $V = V_{PD}$ line with the relative EOS curves. The two values are shown dashed lines on the Fig. 3. Our crude estimate gives 26 GPa for SrBiO3 and 34 GPa for BaBiO3; the agreement with the transition pressure is remarkable for SrBiO3 (25 GPa), but apparently quite bad for BaBiO3 (87 GPa). However, we recall that in BaBiO3 a clustered phase, in which only half of the Bi atoms are arranged in a regular octahedral environment, is predicted to occur in-between the perovskite and the distorted structure, shifting the transition to fully distorted structures to 87 GPa. If one disregards the clustered phase, the transition from perovskite to distorted structure occurs at around 45 GPa, which is in fair agreement to the 34 GPa value, predicted from the ideal cubic model.

IV. CONCLUSIONS

In conclusion, in this work we studied the pressure-behaviour of three rare-earth bismuthates ABIO3 (A=Ba, Sr, Ca), using ab-initio crystal structure prediction and hybrid functional calculations. Similarly to what previously observed in BaBiO3, we find that charge disproportionation is robust and not suppressed by pressure in all ABIO3 compounds, which also all remain insulators up to 100 GPa. The charge disproportionation between $Bi^{3+}$ and $Bi^{5+}$, estimated by Bader charge analysis, is much higher than what predicted by usual methods based on the DOS, starting from around 0.5 $e^{-}$ at ambient pressure and going up to 0.7 $e^{-}$ for the highly distorted high-pressure structures.

Indeed, the tendency to charge disproportionation becomes stronger with increasing pressure and has a big influence on the crystal structure; in fact, all compounds undergo a transition from perovskite structure to a highly distorted structure (PD transition); in BaBiO3, this happens through a transition to an intermediate clustered phase, whose presence shifts the PD transition to higher pressures, with respect to the value estimated on the basis of chemical pressure.

The formation of distorted structures is explained by a steric effect, combined with the mixed-valence behavior of bismuth; distorted structures have a higher density (more efficient packing) than any variant of the perovskite structure, and this permits to reduce the $pV$ contribution to the enthalpy which is dominant at high pressures. In the distorted structures, a more efficient packing is achieved by allowing the coordination number to increase beyond the value 6 for the characteristic of the perovskite structure; this tendency, combined with that to charge disproportionation, means that it is not possible to form any symmetric structure under this circumstances.
V. COMPUTATIONAL DETAILS

To construct the high-pressure phase diagram, candidate structures with 10, 20 and 40 atoms per unit cell at 0 GPa, 50 GPa and 100 GPa were generated using the USPEX code for evolutionary crystal structure prediction. For each group of structures, generated by a separate USPEX run, we chose 5 lowest in enthalpy to perform a final accurate structure relaxation. The structure relaxations were performed allowing atoms relaxations and change of the cell shape, but the volume was fixed. Each structure was then relaxed on a grid of at least 9 volumes, chosen between the average volumes corresponding to 0 and 100 GPa. The pressures of the relaxed structures were estimated from the stress tensor. The resulting pressure vs volume relation were then interpolated analytically; from the interpolation curves, we obtained the transition pressures used to derive the final phase diagram shown in Fig. 1.

We used density functional theory (DFT) in the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof functional to calculate the total energies and perform structural optimization, as implemented in the VASP package using projector augmented wave method (PAW) pseudopotentials. The hybrid HSE functional (Heyd-Scuseria-Ernzerhof) was used only to compute electronic spectra, in particular for the DOS calculations (Fig. 3) and for calculation of band gaps (Fig. 4). The energy cutoff value was set to 500 eV and Γ-centered Monkhorst-Pack grid with the reciprocal-space resolution 0.04 Å⁻¹ was used for the GGA for structural relaxation and 0.01 Å⁻¹ for total energy calculation. For calculations where HSE functional was used the reciprocal-space resolution was 0.04 Å⁻¹.

The neighbors analysis was performed with the help of the Chemenv module from the Pymatgen package. Chemenv provides routines to obtain the best fit of the coordination environment polyhedron for a specific atom and this information was used to estimate the number of oxygen neighbors for each bismuth atom in Fig. 6.

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Figure 3. (color online) Total and atom-projected DOS for $ABiO_3$ compounds before and after the PD transition: 22 GPa for CaBiO$_3$, 25 GPa for SrBiO$_3$ and 45 GPa for BaBiO$_3$, calculated with the HSE functional; the structures were optimized at the PBE level. Bi atoms are divided into formal $\text{Bi}^{3+}$ and $\text{Bi}^{5+}$ valences. For the sake of clarity the Bi-DOS is multiplied by a factor 15.

Figure 4. (color online) Band gaps for the most stable structures of $ABiO_3$ compounds as a function of pressure. Each symbol represents a specific structure, as defined in the caption of Fig. 1; the filling indicates whether the structure is perovskite-like (filled symbol) or distorted (empty symbol). Lines are meant as a guidance to the eye.

Figure 5. (color online) Difference between maximum and minimum charge ($\Delta \rho$) located on bismuth atoms w.r.t pressure, obtained using Bader analysis. Note that the Bader charge analysis yields sensibly higher values than the estimate based on the partial DOS estimate used in our previous paper. The meaning of the symbols is the same as in Fig. 4.
Figure 6. *(color online)* Average number of Bi nearest neighbors as a function of pressure. The meaning of the symbols is the same as in Fig. 4.

Figure 7. *(color online)* Average BiO bond length as a function of pressure. The meaning of the symbols is the same as in Fig. 4.

Figure 8. *(color online)* Equation of state for $A$BiO$_3$ compounds in the ideal cubic perovskite structure, used as a model to estimate the shift of the PD transition line due to the chemical pressure, showed by dashed lines in Fig. 1. The PD transition at 22 GPa for CaBiO$_3$ is taken as a reference point to estimate a common volume for the transition (see text). Lines are meant as a guidance for the eye.
is based on evolutionary algorithm approach and
its main idea is to form a population of crystal structures
which are evolved under various evolutionary operators im-
imitating biological ideas of mutation, reproduction, recom-
bination and selection which minimize the fitness function
represented by an enthalpy of the system, calculated us-
ab-initio methods used in our work. Although we report differ-
ent distorted structures for different ABiO$_3$ compounds, this does not necessarily imply
that they are different in experiment: it might be that due
to the too small size of the unit cell, we reproduce different
parts of some more complex and bigger distorted structural
motif.

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28 It worth to note that such drastic distortions may be indicator of some critical phenomena that happens at high pressure for ABiO$_3$ compounds, like transition to amorphous-like state or chemical decomposition, that cannot be explained by ab-initio methods used in our work.

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