Phase Transitions and Electric Properties of PbBr$_2$ under High Pressure: A First-Principles Study

Lihua Yang$^{1,2}$, Yukai Zhang$^1$, Yanli Chen$^1$, Xin Zhong$^1$, Dandan Wang$^1$, Lin Fan$^1$, Jihui Lang$^1$, Xin Qu$^1, *$, and Jinghai Yang$^1, *$

1 Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, College of Physics, Jilin Normal University, Siping 136000, China
2 State Key Laboratory of Integrated Optoelectronics, College of Materials Science and Engineering, Jilin University, Changchun 130012, China
* Correspondence: quxin5158163.com (X.Q.); jhyang1@jlnu.edu.cn (J.Y.)

Abstract: PbBr$_2$ has recently attracted considerable attention as a precursor for lead halide perovskite-based devices because of its attractive properties. It is known that pressure can modify the chemical and physical properties of materials by altering the distance between atoms in the lattice. Here, a global structure-searching scheme was used to explore the high-pressure structures of PbBr$_2$, whose structures and properties at high pressure are still far from clear. Three new phases of PbBr$_2$ were predicted in the pressure range of 0–200 GPa, and the pressure-driven phase transition sequence of orthorhombic Pnma (0–52 GPa) $\rightarrow$ tetragonal I4/mmm (52–80 GPa) $\rightarrow$ orthorhombic Cmca (80–153.5 GPa) $\rightarrow$ orthorhombic Immm (153.5–200 GPa) is proposed. Electronic calculations indicate a semiconductor-to-metallic transition of PbBr$_2$ in the Cmca phase at $\sim$120 GPa. Our present results could be helpful in improving the understanding of fundamental physical properties and provide insights to modulate the structural and related photoelectric properties of PbBr$_2$.

Keywords: high pressure; structure prediction; simulation; structural evolution; lead halide

1. Introduction

Lead bromide (PbBr$_2$) is drawing attention due to significant scientific and technological applications. The presence of Pb with a high effective atomic number (Z$_{\text{eff}}$ = 82) enables PbBr$_2$ to have a superior absorption ability for high-energy photons, so that PbBr$_2$ could be applied in X-ray or $\gamma$-ray detection [1–3]. Due to its good acousto-optic merit and wide transmission range, PbBr$_2$ has been applied in acousto-optic devices [4–7]. The crystal growth, purification, and optical and acoustic character of PbBr$_2$ have been studied over the past few decades [6–10]. Recently, PbBr$_2$ has been used extensively to prepare perovskite-based devices, such as the hybrid perovskites solar cells [11–13], photodetectors [14], led light-based devices [15], photocatalysts of antibiotics [16] and luminescent complexes in solvents [17,18].

It is known that pressure can alter the chemical and physical properties of materials as it can adjust the distance between atoms in the lattice [19–24]. At ambient conditions, PbBr$_2$ is a semiconductor material and crystallizes in a cotunnite phase (Pnma, Z = 4) similar to many other AB$_2$ compounds [9,10,25,26]. Theoretical and experimental studies on the electronic properties and structural transition sequences under high pressure for PbBr$_2$ are less investigated, hindering the in-depth exploration of the chemical and physical properties of PbBr$_2$ under compression. Thus, it is essential to investigate the structural evolution of PbBr$_2$ under pressure for the further design of lead halide perovskite photovoltaics.

In this work, we explored the structures of PbBr$_2$ by the well-known CALYPSO structure searches method, combined with first-principles calculations at a wide pressure range of 0–200 GPa. Our results show that the pressure-driven structural evolution of PbBr$_2$ is orthorhombic Pnma $\rightarrow$ tetragonal I4/mmm $\rightarrow$ orthorhombic Cmca $\rightarrow$ orthorhombic...
Materials 2022, 15, 8222 2 of 8

Immm phase with transition pressures of 52, 80 and 153.5 GPa, respectively. We further investigated the PbBr₂ electronic properties under high pressure. Strikingly, the phase transition is accompanied by a semiconductor-to-metallic transition. Our results will advance the understanding of the structure and electronic properties of PbBr₂ under extreme conditions.

2. Materials and Methods

Structure searches for PbBr₂ were carried out by the CALYPSO method (by registering at http://www.calypso.cn, accessed on 5 June 2013) [27–29], which was verified successfully by many studies [30–37]. Each generation contained 50 structures, and the first generation was produced randomly with symmetry constraints. All structures were locally optimized using the VASP code [38]. Local optimizations performed during structure search were undertaken with the conjugate gradients method and were stopped when enthalpy changes became smaller than 1 × 10⁻⁵ eV per cell. Sixty percent of the lowest-enthalpy structures of each generation were used to produce the structures in the next generation by local Particle Swarm Optimization techniques, and the remaining 40% of structures were randomly generated within symmetry constraints to enhance structural diversity. During the structure searches, each newly generated structure was subjected to structural optimization at target pressures to obtain local-minimum configurations. All structure optimization, enthalpy and electronic properties calculations adopt the VASP code with the generalized gradient approximation functional (Perdew–Burke–Ernzerh) [39]. We employ the projector augmented wave [40] scheme to treat the valence electrons of Pb and Br as 5d¹⁰ 6s² 6p² and 3d¹⁰ 4s² 4p⁵. A total of 1000–1200 structures were generated for each structure search calculation with an energy cutoff of 310 eV. To ensure convergence of the calculated data, a kinetic energy cutoff of 400 eV and dense k-point sampling with a grid spacing of 0.2 Å⁻¹ were employed. We used the PHONOPY code to ensure dynamical stabilities of the predicted PbBr₂ structures [25]. Electron localization functions (ELFs) were drawn using VESTA software [41].

3. Results and Discussion

To discover stable structures of PbBr₂ at high pressure, we executed systematic structural searches with 1–4 formula units at 0, 20, 50, 100, 150 and 200 GPa. According to our simulations, four energetically stable PbBr₂ phases were found and are shown in Figure 1a–d. At 0 and 20 GPa, we reproduced the experimental Pnma structure (4 f.u., Z = 4). The unit-cell parameters of the predicted Pnma structure are very close to the experiment data [6,10], demonstrating the validity of the simulated method adopted here. As shown in Figure 1a, the Pb atom is ninefold coordinated by Br. Both Pb and Br atoms are located on the fourfold 4c site. Above 52 GPa, the already known PbBr₂ with Pnma symmetry transforms into a tetragonal structure with I4/mmm (Z = 2) symmetry, accompanied by the nearest Br–Br distances shortened from 3.26 Å (at 20 GPa) to 2.88 Å (at 60 GPa). In the I4/mmm structure, Pb and Br atoms occupy the 2b site and 4e site, respectively. Within this structure, each Pb atom is tenfold coordinated by Br, forming a PbBr₁₀ square prism with a double cap. At 60 GPa, the distance from the central Pb atom to the side Br1 atom and capped Br2 atoms of the prism is 2.836 Å and 3.022 Å, respectively. The Pnma and I4/mmm structures of PbBr₂ are also predicted to exist in PbI₂ and BaI₂ [42,43].

Upon increasing the pressure to 80 GPa, PbBr₂ adopts an orthorhombic Cmca structure with Z = 8. This structure can be seen as symmetry lowering of the I4/mmm structure. Within the Cmca structure (Figure 1c), Pb and Br atoms occupy the Wyckoff 8f site and 16g site, respectively, and the nearest Br–Br is 2.73 Å at 100 GPa. At a pressure above 153.5 GPa, an orthorhombic Immm (Z = 8) phase was found to be most stable up to 200 GPa. Significantly, the current PbBr₂ Immm structure differs from the Immm structure found in PbI₂ (Immm-I) [42]. While the former structure (Figure 1d) contains two distinct Pb atoms occupying the 4i and 4h sites, and four Br atoms occupying 2b, 2d, 4g, and 8l, respectively, the later has 2 f.u. in a unit cell with the Pb and I atoms occupying the Wyckoff 2d site and
4f site (the enthalpy difference of two Immm phases was calculated in Figure 2a). Within the Immm structure of PbBr$_2$, the Pb atoms are tenfold coordinated, and the nearest Br–Br is 2.57 Å at 200 GPa. In conclusion, the Br–Br distances in the four stable PbBr$_2$ structures are much smaller than those in pure Br$_2$ (2.27 Å), indicating that no Br–Br covalent bond is formed.

Figure 1. Crystal structures of stable PbBr$_2$: (a) Pnma at 20 GPa, (b) I4/mmm at 60 GPa, (c) Cmca at 100 GPa, and (d) Immm at 200 GPa.

We calculated the enthalpy difference ($\Delta H$) of four stable PbBr$_2$ phases relative to I4/mmm PbBr$_2$, as shown in Figure 2a. Several structures in a previous study on lead halide compounds [42] were also considered. Obviously, the four PbBr$_2$ structures we searched have the lower enthalpies. The changes in volume as a function of pressure of the predicted PbBr$_2$ are also plotted in Figure 2b. The continuous change of unit cell volume of PbBr$_2$ with pressure suggests a second-order structural phase transition. Our work suggests that PbBr$_2$ follows the structural transition order of Pnma (0–52 GPa) → I4/mmm (52–80 GPa) → Cmca (80–153.5 GPa) → Immm (153.5–200 GPa). Our phonon
calculations demonstrate the dynamic stability of all these predicted PbBr₂ structures, as shown in Figure 3. The detailed structural parameters and calculated phonon spectra of the predicted PbBr₂ phases are shown in Table 1.

Figure 3. Phonon dispersion curves of stable PbBr₂: (a) Pnma at 20 GPa, (b) I4/mmm at 60 GPa, (c) Cmca at 100 GPa, and (d) Immm at 200 GPa.

Table 1. Lattice parameters and atomic coordinates of a conventional unit cell of PbBr₂.

| Phase   | Z | Lattice (Å) | Atom      | X   | Y   | Z   |
|---------|---|-------------|-----------|-----|-----|-----|
| Pnma    | 4 | a = 8.04246 | Pb(4c)    | 0.734| 0.750| 0.910|
| 0 GPa   |   | b = 4.76121 | Br1(4c)   | 0.516| 0.750| 0.162|
|         |   | c = 9.66722 | Br2(4c)   | 0.358| 0.250| 0.418|
| I4/mmm  | 2 | a = b = 3.426| Pb(2a)    | 0.000| 0.000| 0.000|
| 60 GPa  |   | c = 8.993   | Br(4e)    | 0.000| 0.000| 0.336|
| Cmca    | 8 | a = 8.548   | Pb(8f)    | 0.000| 0.790| 0.875|
| 100 GPa |   | b = 4.679   | Br(16g)   | −0.166|0.295|0.875|
|         |   | c = 9.295   | α = β = γ = 90 |
| Immm    | 8 | a = 3.598   | Pb(4i)    | 0.000| 0.000| 0.241|
| 200 GPa |   | b = 11.177  | Br1(2d)   | 0.500| 0.000| 0.500|
|         |   | c = 7.594   | Br2(4g)   | 0.000| 0.837| 0.000|
|         |   | α = β = γ = 90 | Br3(8l) | 0.500| 0.833| 0.253|
|         |   |             | Br4(2b)   | 0.500| 0.000| 0.000|

In order to further research the bonding properties of PbBr₂ under compression, we investigated the ELF of four stable PbBr₂ phases. All phases share similar features. We present the ELF of the I4/mmm phase in Figure 4 as a representative. The blue color corresponding to the ELF value < 0.5 is mostly around Pb atoms, indicating the electron shortage of Pb and electron transfer from Pb to Br. Because the ELF map does not show electron localization at the lattice gap, the bonding type between Pb and Br is mainly ionic. The isosurface of ELF with a value of 0.7 (Figure 4b) also indicates an electronic consumption near Pb atoms and cumulation around Br atoms, showing the charge transfer from Pb to Br, associated with the Pb–Br ionic bond.
present the ELF of the I4/mmm phase in Figure 4 as a representative. The blue color corresponding to the ELF value < 0.5 is mostly around Pb atoms, indicating the electron shortage of Pb and electron transfer from Pb to Br. Because the ELF map does not show electron localization at the lattice gap, the bonding type between Pb and Br is mainly ionic. The isosurface of ELF with a value of 0.7 (Figure 4b) also indicates an electronic consumption near Pb atoms and cumulation around Br atoms, showing the charge transfer from Pb to Br, associated with the Pb–Br ionic bond.

Figure 4. (a) 2D ELF plot through the (1–10) plane and (b) isosurface of the ELF plot with a value of 0.7 for I4/mmm PbBr2 at 60 GPa. Big spheres represent Pb atoms; small spheres denote Br atoms.

We calculated the electronic band and partial density of states (PDOS) of the four predicted structures. The Pnma phase is a semiconductor with an indirect bandgap $E_g = 2.11$ eV, where the Pb-6p and Br-5p states dominate the valence band (VB) edge, and an anti-bonding hybridization of the Pb-6s and Br-5p states controls the conduction band (CB) edge, as shown in Figure 5a. The bonding character of the I4/mmm phase is similar to that in the Pnma structure, e.g., the band structure calculated at 60 GPa also shows an indirect band gap ($E_g = 0.69$ eV). The I4/mmm structure remains a semiconductor at the pressure stability interval (52–80 GPa). For the Cmca structure of PbBr2, the calculated band structures at 80, 120 and 140 GPa show that a semiconductor–metal transition occurs at ~120 GPa, because the CB extends across the Fermi level (Figure 5c–e). It can be seen that lead bromide metallizes at a higher pressure than lead iodide (~27 GPa). In the high-pressure Immm phase of PbBr2, both the VB and CB extend across the Fermi level, and the metallic nature of PbBr2 persists up to 200 GPa.
4. Conclusions

We studied the pressure-driven structural transformation and electronic properties of PbBr₂ up to 200 GPa. The structural evolution of PbBr₂ is orthorhombic Pnma → tetragonal I4/mmm → orthorhombic Cmca → orthorhombic Immm phase with transition pressures of 52, 80 and 153.5 GPa, respectively. Electronic calculations indicate that Pnma and I4/mmm phases are semiconductors, and a semiconductor-to-metallic transition of PbBr₂ was found in the Cmca phase at ~120 GPa. The Immm phase maintains metallic properties throughout the pressure stabilization range. Our results will stimulate further studies on the behavior of AB₂-type halides under extreme conditions.

Author Contributions: Investigation, Y.Z. and L.F.; data curation, D.W. and X.Z.; writing—original draft preparation, L.Y.; writing—review and editing, X.Q. and Y.C.; supervision, L.Y. and J.Y.; funding acquisition, J.L. All authors have read and agreed to the published version of the manuscript.
Funding: This research was funded by the National Natural Science Foundation of China, grant number 11904129, 22078124 and 61904066; the Program for the Development of Science and Technology of Jilin Province, grant numbers YDZJ202101ZTS065 and 202002015JC; and the Research Project of the “13th Five-Year Plan” of Jilin Provincial Education Department, grant numbers JJKH20220423KJ.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Yanagida, T.; Fujimoto, Y.; Yoshikawa, A.; Yokota, Y.; Kamada, K.; Pejchal, J.; Chani, V.; Kawaguchi, N.; Fukuda, K.; Uchiyama, K.; et al. Development and Performance Test of Picosecond Pulse X-ray Excited Streak Camera System for Scintillator Characterization. Appl. Phys. Express 2010, 3, 056202. [CrossRef]
2. Torres, O.G.; Gordillo, G.; Plazas, M.C.; Tellez, D.A.L.; Roa-Rojas, J. Optical features of PbBr2 semiconductor thin films for radiation attenuation application. J. Mater. Sci. Mater. Electron. 2021, 32, 16937–16944. [CrossRef]
3. Nikl, M. Scintillation detectors for X-rays. Meas. Sci. Technol. 2006, 17, R37–R54. [CrossRef]
4. Tubbs, M.R. The optical properties and chemical decomposition of halides with layer structures. I. crystal structures, optical properties, and electronic structure. Phys. Status Solidi 1972, 49, 11–50. [CrossRef]
5. Kusumoto, H.; Kaito, T.; Yanagiya, S.-I.; Mori, A.; Inoue, T. Growth of single crystals of PbBr2 in silica gel. J. Cryst. Growth 2005, 277, 536–540. [CrossRef]
6. Kaito, T.; Yanagiya, S.-I.; Mori, A.; Kurumada, M.; Kaito, C.; Inoue, T. Characteristic nanocrystallite growth of PbBr2 in a magnetic field in gel. J. Cryst. Growth 2006, 294, 407–410. [CrossRef]
7. Kaito, T.; Inoue, T.; Yanagiya, S.; Mori, A.; Masaki, K. Melt growth and characterization of PbBr2 single crystals. J. Cryst. Growth 2005, 275, e721–e726. [CrossRef]
8. Ahmad, Z.; Mishra, A. Growth of PbBr2 microrods with unique structure and surface morphology. J. Mater. Sci. Mater. Electron. 2020, 31, 4672. [CrossRef]
9. Girgis, S.Y.; Mady, K.A. Electrical conductivity of vacuum-deposited lead bromide layers. J. Mater. Sci. Lett. 1986, 5, 1091–1094. [CrossRef]
10. Varshney, S.; Chi, L.; Singh, C.V.; Nogami, J. Atomic structure of PbBr2 thick films on Ag (111). Solid State Commun. 2022, 343, 114651. [CrossRef]
11. Mutalikdesai, A.; Ramasesha, S.K. Emerging solar technologies: Perovskite solar cell. Resonance 2017, 22, 1061–1083. [CrossRef]
12. Cleveland, I.J.; Tran, M.N.; Dey, A.; Aydil, E.S. Vapor deposition of CsPbBr3 thin films by evaporation of CsBr and PbBr2. J. Vac. Sci. Technol. A 2021, 39, 043415. [CrossRef]
13. Ren, Q.; Ding, L.-Y.; Chen, F.-S.; Cheng, R.-P.; Xu, D. The optical properties of lead bromide crystals. J. Mater. Sci. Lett. 1997, 16, 1247–1248. [CrossRef]
14. Liu, Y.; Zhang, Y.; Yang, Z.; Feng, J.; Xu, Z.; Li, Q.; Hu, M.; Ye, H.; Zhang, X.; Liu, M.; et al. Low-temperature-gradient crystallization for multi-inch high-quality perovskite single crystals for record performance photodetectors. Mater. Today 2019, 22, 67–75. [CrossRef]
15. Lan, J.; Luo, L.; Wang, M.; Li, F.; Wu, X.; Wang, F. One pot gram-scale synthesis of CsPbBr3 nanocrystals and their application in green LED. J. Lumin. 2019, 210, 464–471. [CrossRef]
16. Zhao, Y.; Wang, Y.; Liang, X.; Shi, H.; Wang, C.; Fan, J.; Hu, X.; Liu, E. Enhanced photocatalytic activity of Ag-CsPbBr3/CN composite for broad spectrum photocatalytic degradation of cephalosporin antibiotics 7-ACA. Appl. Catal. B Environ. 2019, 247, 57–69. [CrossRef]
17. Chin, S.-H.; Choi, J.W.; Hu, Z.; Mardegan, L.; Sessolo, M.; Bolink, H.J. Tunable luminescent lead bromide complexes. J. Mater. Chem. C 2020, 8, 15996–16000. [CrossRef]
18. Yin, J.; Zhang, Y.; Bruno, A.; Soci, C.; Bakr, O.M.; Brédas, J.-L.; Mohammed, O.F. Intrinsic Lead Ion Emissions in Zero-Dimensional CsPbBr3 Nanocrystals. ACS Energy Lett. 2017, 2, 2805–2811. [CrossRef]
19. Liu, Y.; Wang, R.; Wang, Z.; Li, D.; Cui, T. Formation of twelve-fold iodine coordination at high pressure. Nat. Commun. 2012, 13, 412. [CrossRef] [PubMed]
20. Zhang, L.; Wang, Y.; Lv, J.; Ma, Y. Materials discovery at high pressures. Nat. Rev. Mater. 2017, 2, 17005. [CrossRef]
21. Liu, R.; Xu, D.; Yao, Z.; Niu, S.; Liu, B. The New High-Pressure Phases of Nitrogen-Rich Ag–N Compounds. Materials 2022, 15, 4986. [CrossRef] [PubMed]
22. Li, S.; Wang, H.; Sun, W.; Lu, C.; Peng, F. Superconductivity in compressed ternary alkaline boron hydrides. Phys. Rev. B 2022, 105, 224107. [CrossRef]
23. Yang, L.; Qu, X.; Zhong, X.; Wang, D.; Chen, Y.; Lang, J.; Liu, C.; Sun, B.; Yang, J. The unconventionally stoichiometric compounds in the Na–K system at high pressures. Comput. Mater. Sci. 2021, 200, 110818. [CrossRef]
24. Qu, X.; Yang, L.; Lv, J.; Xie, Y.; Yang, J.; Zhang, Y.; Wang, Y.; Zhao, J.; Chen, Z.; Ma, Y. Particle Swarm Predictions of a SrB₈ Monolayer with 12-Fold Metal Coordination. *J. Am. Chem. Soc.* 2022, 144, 11120–11128. [CrossRef]

25. Togo, A.; Oba, F.; Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Phys. Rev. B Condens. Matter Mater. Phys.* 2008, 78, 134106. [CrossRef]

26. Raman, A.; Steinfink, H. Crystal chemistry of AB₂ structures. *Inorg. Chem.* 1967, 6, 1789–1791. [CrossRef]

27. Wang, Y.; Lv, J.; Ma, Y.; Cui, T.; Zou, G. Superconductivity of MgB₂ under Ultra high Pressure: A First-Principles Study. *Phys. Rev. B* 2009, 80, 092505. [CrossRef]

28. Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. CALYPSO: A Method for Crystal Structure Prediction. *Comput. Phys. Commun.* 2012, 183, 2063–2070. [CrossRef]

29. Lv, J.; Wang, Y.; Zhu, L.; Ma, Y. Particle-swarm structure prediction on clusters. *J. Chem. Phys.* 2012, 137, 084104. [CrossRef]

30. Lu, W.; Liu, S.; Liu, G.; Hao, K.; Zhou, M.; Gao, P.; Wang, H.; Lv, J.; Gou, H.; Yang, G.; et al. Disproportionation of SO₂ at High Pressure and Temperature. *Phys. Rev. Lett.* 2022, 128, 106001. [CrossRef]

31. Zhong, X.; Sun, Y.; Iitaka, T.; Xu, M.; Liu, H.; Hemley, R.J.; Chen, C.; Ma, Y. Prediction of Above-Room-Temperature Superconductivity in Lanthanide/Actinide Extreme Superhydrides. *J. Am. Chem. Soc.* 2022, 144, 13394–13400. [CrossRef]

32. Zhu, L.; Liu, H.; Pickard, C.J.; Zou, G.; Ma, Y. Reactions of Xenon with Iron and Nickel Are Predicted in the Earth’s Inner Core. *Nat. Chem.* 2014, 6, 644–648. [CrossRef]

33. Li, Y.; Hao, J.; Liu, H.; Li, Y.; Ma, Y. The Metallization and Superconductivity of Dense Hydrogen Sulfide. *J. Chem. Phys.* 2014, 140, 174712. [CrossRef]

34. Li, Y.; Wang, L.; Liu, H.; Zhang, Y.; Hao, J.; Pickard, C.J.; Nelson, J.R.; Needs, R.J.; Li, W.; Huang, Y.; et al. Dissociation Products and Structures of Solid H₂S at Strong Compression. *Phys. Rev. B* 2016, 93, 020103. [CrossRef]

35. Li, X.; Zhang, X.; Bergara, A.; Gao, G.; Liu, Y.; Yang, G. Superconducting LaP₂H₂ with graphenelike phosphorus layers. *Phys. Rev. B* 2022, 105, 024504. [CrossRef]

36. Yan, X.; Ding, S.; Zhang, X.; Bergara, A.; Liu, Y.; Wang, Y.; Zhou, X.-F.; Yang, G. Enhanced superconductivity in CuH₂ monolayers. *Phys. Rev. B* 2022, 106, 014514. [CrossRef]

37. Lv, J.; Wang, Y.; Zhu, L.; Ma, Y. Predicted Novel High–Pressure Phases of Lithium. *Phys. Rev. Lett.* 2011, 106, 015503. [CrossRef]

38. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, 11169. [CrossRef]

39. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865. [CrossRef]

40. Blochl, P.E. Projector Augmented–Wave Method. *Phys. Rev. B* 1994, 50, 17953. [CrossRef]

41. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* 2011, 44, 1272–1276. [CrossRef]

42. Yang, L.; Zhang, Y.; Wang, J.; Wang, Y.; Yu, W.W. Pressure-induced phase transitions of lead iodide. *RSC Adv.* 2016, 6, 84604–84609. [CrossRef]

43. Wei, S.; Liu, H. High-Pressure Structures and Superconductivity of Barium Iodide. *Materials* 2022, 15, 522. [CrossRef]