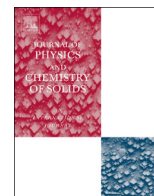




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## Novel high-pressure crystal structures of boron trifluoride

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## ABSTRACTS

This study systematically investigated the high-pressure crystal structures of solid trifluoride (BF<sub>3</sub>) using first principle structure searches and several high-pressure phases were predicted. We found that the coordination of B atoms increased from 3 to 4 at 11 GPa, and to 6 at 160 GPa, while all the F atoms were bridge bonding at a sufficiently high pressure, from terminal bonding. Further calculations of the electronic properties showed that solid BF<sub>3</sub> remained insulating up to the highest pressure considered, i.e., 300 GPa. Phonon calculations indicated that all the predicted structures of BF<sub>3</sub> are dynamically stable under high pressure. These results show that pressure plays an important role in the changing chemical environments of elements, thereby improving our understanding of the evolution of structure and bonding with compression in other molecular systems, particularly in other boron trihalides.

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## 1. Introduction

The study of molecular systems at high pressures has been a central topic for fundamental physics and chemistry, as well as planetary sciences [1,2]. As the pressure increases, molecular solids tend toward polymerization because the effect of pressure  $\times$  volume ( $PV$ ) on solids progressively modifies the Gibbs free energy of the system, where  $G=E+PV-TS$  ( $G$ ,  $E$ ,  $P$ ,  $V$ ,  $T$  and  $S$  are the Gibbs free energy, total energy, pressure, volume, temperature, and entropy, respectively). A simple physical picture suggests that all molecular systems should collapse to form closed-packed structures with a metallic state at sufficiently high pressures. Recently, boron trihalides have attracted much attention [3–5], particularly because boron trihalides form planar molecular solids at ambient or low pressures and low temperatures. A previous high-pressure study [3] reported a new phase of boron triiodide (BI<sub>3</sub>) at  $\sim$ 6.3 GPa. Remarkably, this newly observed phase was found to be metal at  $\sim$ 23 GPa and it transformed into a superconducting state at  $\sim$ 27 GPa. However, detailed studies of the high-pressure phases of BI<sub>3</sub> are hindered by the incomplete knowledge of its crystal structure, because the x-ray diffraction patterns indicate that iodine atoms can only form face-centered cubic frameworks in this new phase whereas the positions of the boron atoms cannot be determined due to the low x-ray scattering cross sections in experiments. Subsequently, first principles meta-dynamics simulation studies [4] suggested that BI<sub>3</sub> tends to form

dimers with a distorted D<sub>2h</sub> symmetry from molecules under high pressure, which was a reasonable explanation of the experimental measurements. Further theoretical studies predicted that boron trihalides (BX<sub>3</sub>, X=F, Cl, Br, I) would also form the kinetic products of boron trihalide dimers at high pressures [5].

Previous theoretical and experimental studies [3–5] of boron trihalides have focused on the polymerization of planar molecules and their metallization at low pressures. However, the crystal structures of boron trihalides have not been investigated at high pressures, which is important for understanding the changes in the chemical nature of the boron and halogen elements. To systematically explore the structural evolution of trihalides under high pressure and the chemical nature of their bonding with neighboring atoms, we employed BF<sub>3</sub> as a prototype compound and obtained extensive crystal structure predictions to explore the high-pressure phases of solid BF<sub>3</sub> up to 300 GPa using CALYPSO code [6]. Many new high-pressure phases of BF<sub>3</sub> were determined, thereby demonstrating the pressure-induced increase in the coordination of boron atoms from 3 to 4 at 11 GPa, and to 6 at 160 GPa. Our calculations of the electronic band structures showed that solid BF<sub>3</sub> remains insulating up to 300 GPa. These results are helpful for improving our understanding of the high-pressure phase transitions of BF<sub>3</sub>, as well as other molecular systems, particularly other boron trihalides.

## 2. Theoretical details

Our approach was based on the global minimization of the free energy (reduces to enthalpy at 0 K) surfaces by merging the *ab*

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*initio* total energy calculations using the particle swarm optimization (PSO) technique implemented in CALYPSO code [6]. The method we employed has been applied successfully to prediction of the high-pressure crystal structures of dense hydrogen [7], lithium [8], oxygen [9], water ice [10], CO<sub>2</sub> [11], CaH<sub>6</sub> [12], tungsten borides [13], and Bi<sub>2</sub>Te<sub>3</sub> [14], where the blind prediction of the insulating *Aba2-40* (or *oC40*) structure of dense lithium was confirmed by an independent experiment [15]. We performed structure searches in the pressure range of 1–300 GPa (1, 5, 10, 20, 50, 100, 200, and 300 GPa) with up to 16 atoms/cell. In general, the structure search simulations were stopped after generating 1000 structures. The underlying *ab initio* structural relaxations and electronic calculations were performed according to the framework of density functional theory within the Perdew-Burke-Ernzerh [16] as implemented in the Vienna *ab Initio* Simulation Package (VASP) [17,18]. The all-electron projector-augmented wave [19] (PAW) method was utilized where the PAW potentials were taken from the VASP library. A plane wave energy cutoff of

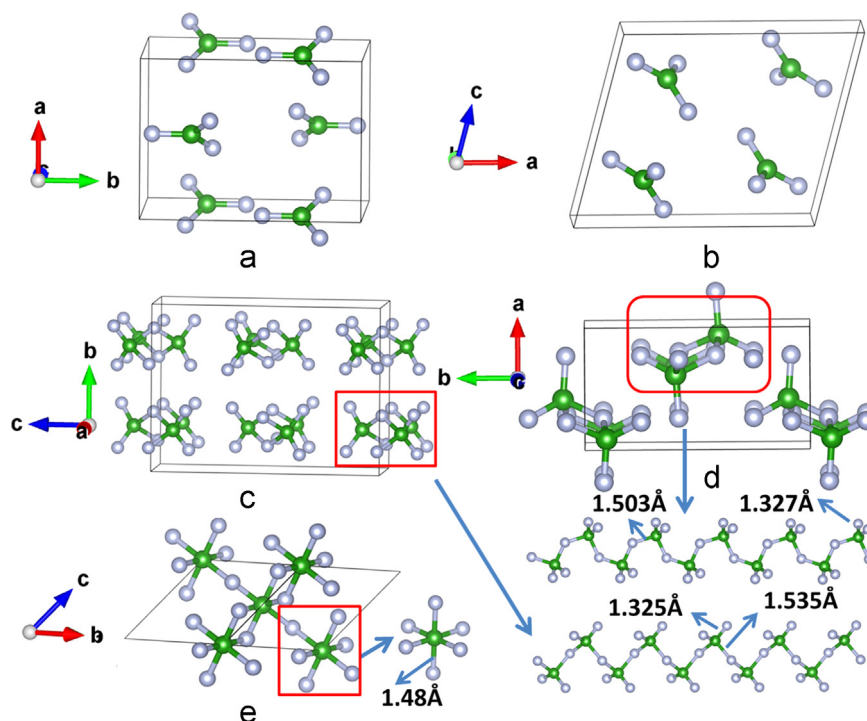
600 eV was employed. We used Monkhorst-Pack [20] *k* grids of  $6 \times 4 \times 6$  for *Pbcn* structure,  $6 \times 10 \times 8$  for *P2<sub>1</sub>/c* structure,  $10 \times 6 \times 4$  for *lbca* structure,  $10 \times 6 \times 10$  for *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* structure,  $12 \times 12 \times 12$  for *R-3c* structure,  $8 \times 8 \times 7$  for *P6<sub>3</sub>/m* structure, and  $12 \times 12 \times 12$  for *P6<sub>3</sub>22* structure to ensure that all the enthalpy calculations converged well. Phonons were calculated using the PHONOPY package [21], where the structures were fully re-optimized.

### 3. Results and discussion

Structure prediction simulations for BF<sub>3</sub> were performed in a pressure range of 1–300 GPa up to 4 formula unit (f.u.) in the simulation cells. At a low-pressure range of 1–10 GPa, *Pbcn* and *P2<sub>1</sub>/c* structures (16 atoms per unit cell) were found to be the most stable structures (Table 1 and Fig. 1). Both structures comprised typical BF<sub>3</sub> planar molecules, which agreed with previous

**Table 1**  
Optimized structural parameters for predicted structures of BF<sub>3</sub>.

Space group	Pressure (GPa)	Lattice parameters (Å or Degree)	Atomic position			
<i>Pbcn</i>	1	a=5.4738	B	0.5	0.72293	0.75
		b=7.4732	F	0.89125	0.68707	1.06593
		c=5.3383	F	0.0	0.04627	0.75
<i>P2<sub>1</sub>/c</i>	5	a=7.1211	B	0.75756	0.58355	0.25617
		b=4.3225	F	0.27616	0.70191	0.80386
		c=5.7808	F	0.07944	0.22844	0.34591
<i>lbca</i>	12	$\beta=75.9741$	F	0.6303	0.72623	0.4311
		a=3.7422	B	0.0	0.25	0.09169
		b=7.4610	F	-0.18693	0.62522	0.34179
<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	100	c=10.1627	F	0.25	0.15341	0.5
		a=3.6481	B	0.39754	0.09621	1.18531
		b=6.6840	F	0.75043	0.24974	0.66740
<i>R-3c</i>	200	c=3.848	F	0.75089	0.41895	1.16104
		a=3.9423	F	0.25056	0.41666	0.83125
		$\alpha=54.2492$	B	0.0	0.0	0.0
			F	-0.75	-0.08376	-0.41624



**Fig. 1.** Predicted structures for BF<sub>3</sub>: *Pbcn* (a), *P2<sub>1</sub>/c* (b), *lbca* (c), *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* (d), and *R-3c* (e). Gray and green spheres indicate F and B atoms, respectively.

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