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Supplementary Information for

The Discovery of a Superhard P-type Transparent Semiconductor: $Al_{2.69}B_{50}$

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Supporting information

Contents

1. General information

The optical image of $Al_{2.69}B_{50}$ is shown in Fig.S1. The EPMA method is often more accurate than EDS and has extensively been used for the light weight elements, like B, N and so on. To quantify the elements ratios in AlBx compound, we employed electron probe micro-analyzer, EPMA (See Table 1). The ration of mole percentage are listed in the Table 1. The atomic ratio of B and Al atoms is 94.938 : 5.062=18.75 : 1, which is same as the calculated single crystal structure atomic ratio B : Al=50 : 2.69=18.59 : 1.

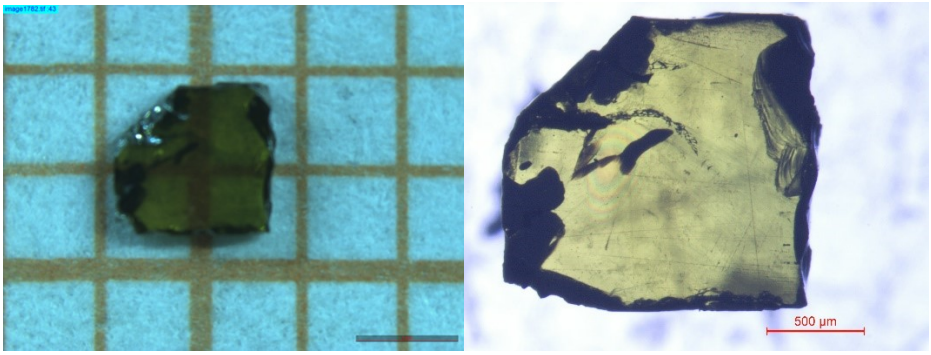

Fig. S1 Optical image of $Al_{2.69}B_{50}$ single crystal.

No.	Elem	Mol%	SD	RSD
1	B	94.938	0.035	0.037
2	Al	5.062	0.035	0.706
Total		100		

Table. S1 Summary of the determined composition for AlBx using electron probe micro-analyzer, EPMA. (Corr Method : ZAF4, Beam Condition [AccV: 15.0kV / BC: 20.0nA / Beam Size: 20µm / SC: 18.3nA])

2. Structure information

Details of occupancy, coordinates and numbers of position of aluminum and born atoms in $Al_{2.69}B_{50}$ are shown in Table S2 (R_1= 5.55 %, wR_2 = 16.33 %). The crystal system is orthorhombic with *Cmma* space group and unit cell parameters are a=12.661 (Å), b=12.337(Å), c=5.093(Å). Density$_{[cal]}$ = 2. 559 g/cm^3. The refined ratio of Al : B from the single crystal X-ray diffraction refinement is 1 : 18.59.

Atom	Label	x	y	z	Occupancy	Mult.	Uiso
AL	AL1	0.00000	-0.25000	1.19030	0.88700	4	0.00950
AL	AL1A	0.00000	-0.25000	1.29500	0.11300	4	0.01100
AL	AL2	0.25000	-0.50000	0.50000	0.34300	4	0.01710
B	B1	0.11643	-0.45404	0.65660	1.00000	16	0.01000
B	B2	0.42673	-0.40680	0.66000	1.00000	16	0.00790
B	B3	0.33904	-0.32553	0.83770	1.00000	16	0.00730
B	B4	0.24298	-0.25000	0.66390	1.00000	8	0.00780
B	B5	-0.12656	-0.25000	0.87190	1.00000	8	0.00780
B	B6	0.20523	-0.37174	0.84600	1.00000	16	0.00780
B	B7	0.00000	-0.37156	0.63030	1.00000	8	0.00670
B	B8	0.50000	-0.50562	0.83630	1.00000	8	0.00810
B	B9	0.00000	-0.25000	0.76280	1.00000	4	0.00670
Details of occupancy, coordinates and numbers of position of aluminum and born atoms in $Al_{2.69}B_{50}$, The crystal system is orthorhombic and *Cmma space group.* Unit cell parameters: a=12. 661 (Å), b=12.337(Å), c=5.093(Å). Density$_{[cal]}$ = 2. 559 g/cm^3 (R_1= 5.55 %, wR_2 = 16.33 %).							

Table. S2 The atom fractional coordinates and crystal information of $Al_{2.69}B_{50}$.

3. Annular-bright-field (ABF) images

Transmission electron microscopy was used to collect images at atomic scale. Fig. S2 shows the images taken along [001], [010], [111] projection directions and HAADF image in [001]-orientation, respectively (insert, atomic structure based on single crystal X-ray diffraction refinement). The atomic structures from refinement match well with these TEM images.

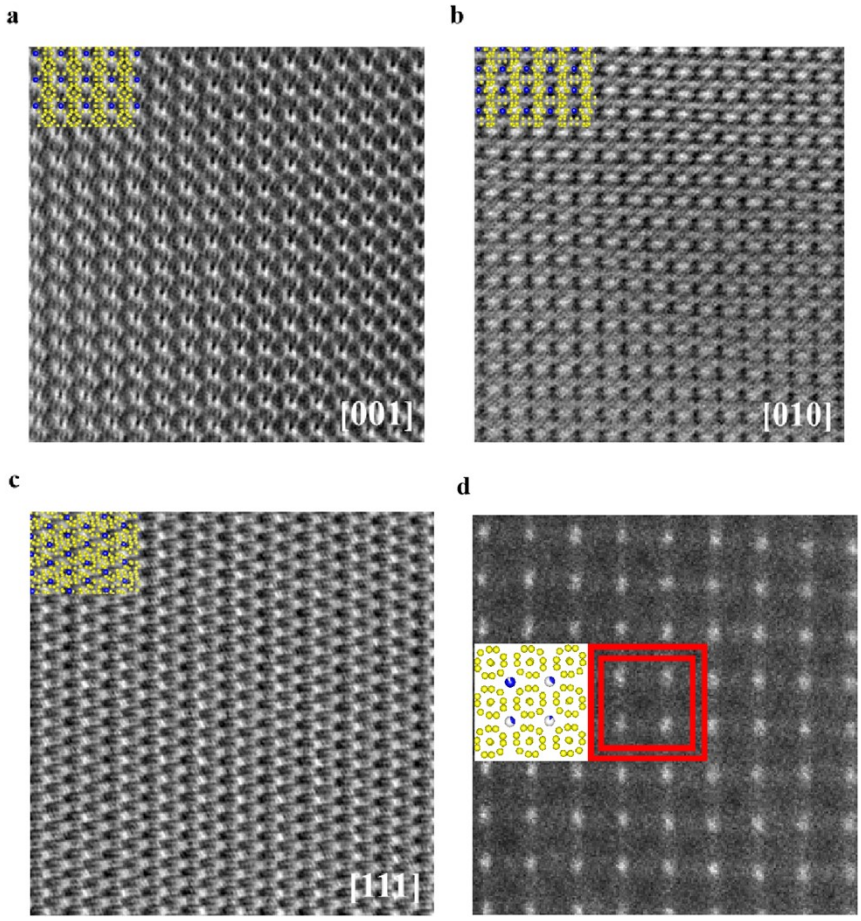

Fig. S2 Annular-bright-field (ABF) images of $Al_{2.69}B_{50}$ along three projection directions: (a) [001]; (b) [010]; (c) [111]. (d) HAADF image in [001]-orientation. The inset images are the schematic crystal structures from single crystal refinement.

4. Mechanical properties of $Al_{2.69}B_{50}$ single crystal

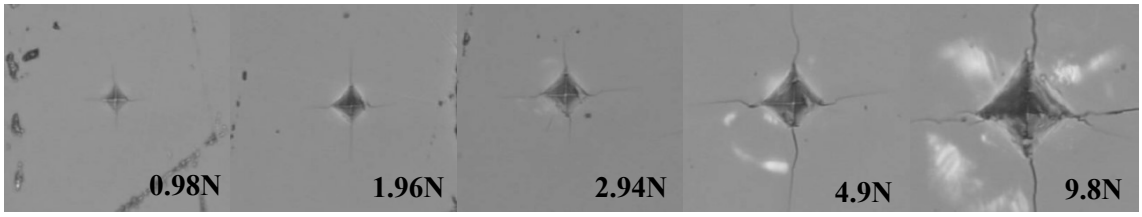

Fig. S3 Indentation photos of hardness test at different load (0.98 N, 1.96 N, 2.94 N, 4.9 N and 9.8 N).

5. Phase and thermal stability

Polycrystalline of $Al_{2.69}B_{50}$ were investigated by high pressure synchrotron X-ray diffraction and Raman spectra at room temperature, as shown in the Fig. S4 and Fig. S5. The gasket in DAC is T_{301} stainless steel, which was pre-indented to thickness of 30 μm and a 150 μm hole was drilled in the center used as the sample chamber. There is no phase and electronic transition within the pressure range up to 40 GPa, and the bulk modulus is 243.4(4) GPa based on the third order Birch-Murnaghan equation of state analysis.

The thermal behavior of the $Al_{2.69}B_{50}$ single crystal (Fig. S6) was analyzed by thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC) in argon atmosphere with a heating rate of 10 K min^{-1} from 0 to 1500 ℃ (the upper limit of our instrument).

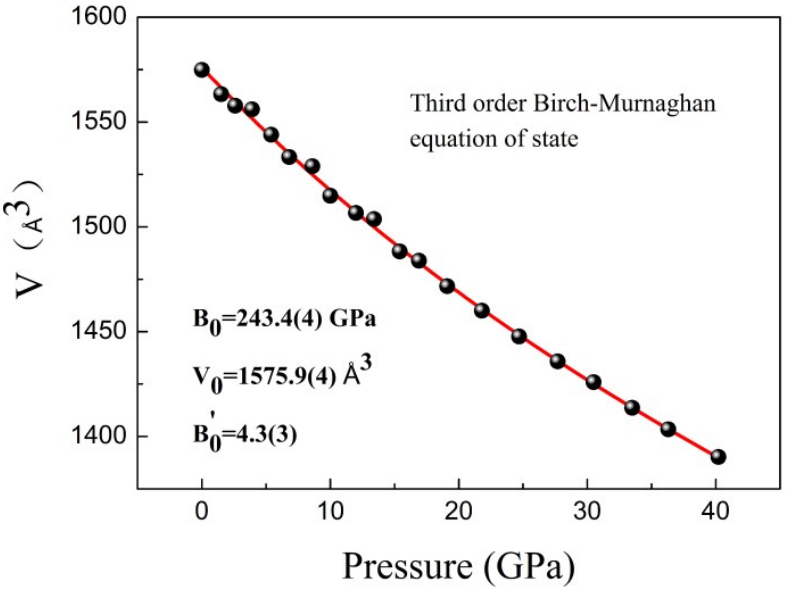

Fig. S4 The pressure-volume data for $Al_{2.69}B_{50}$ and equation of state analysis.

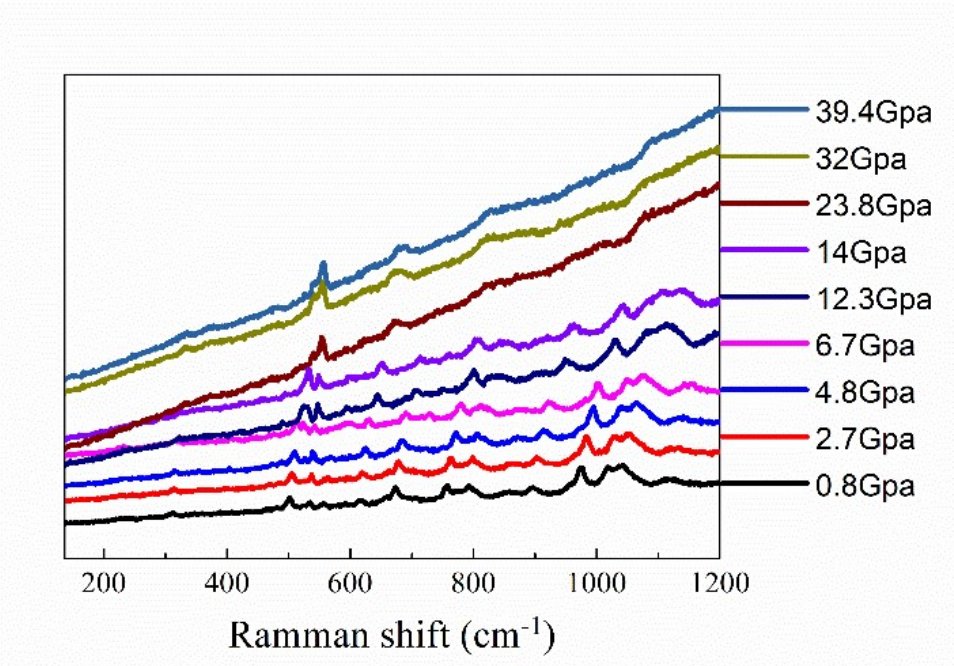

Fig.S5 Raman spectrum of $Al_{2.69}B_{50}$ single crystal at different pressure.

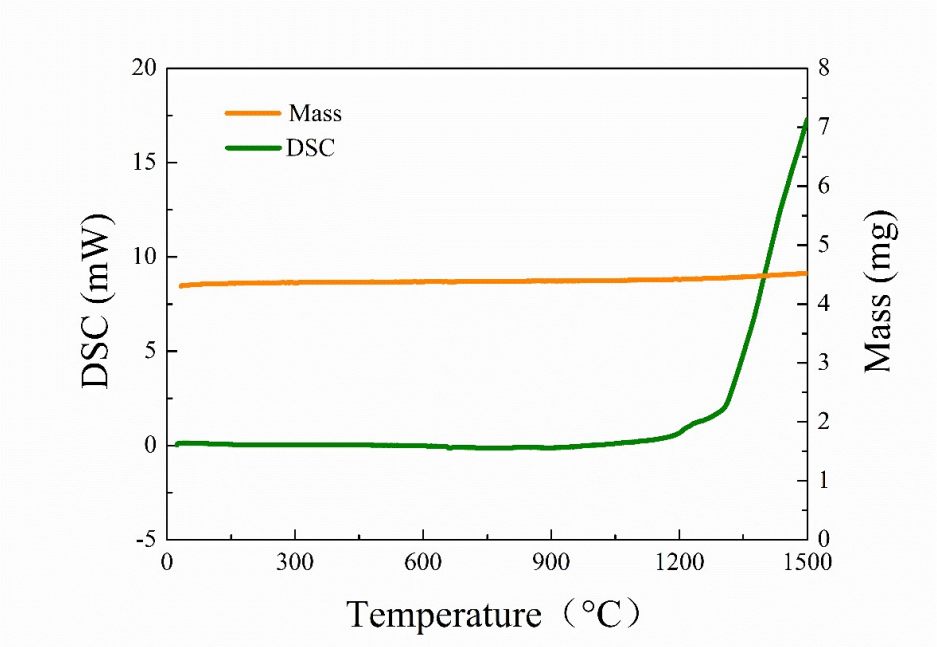

Fig. S6 TG-DTA curves of $Al_{2.69}B_{50}$ single crystal with the protection of argon atmosphere.

6. Photoluminescence (PL) Spectra

We polished the single crystal sample into a cuboid by diamond disks and then measured the PL spectroscopy at room temperature (see the Fig. S7). The $Al_{2.69}B_{50}$ has strong intensity and wide ranges of photon emission in visible ranges, which may be caused by the band gap and numerous B holes in $Al_{2.69}B_{50}$ single crystal.

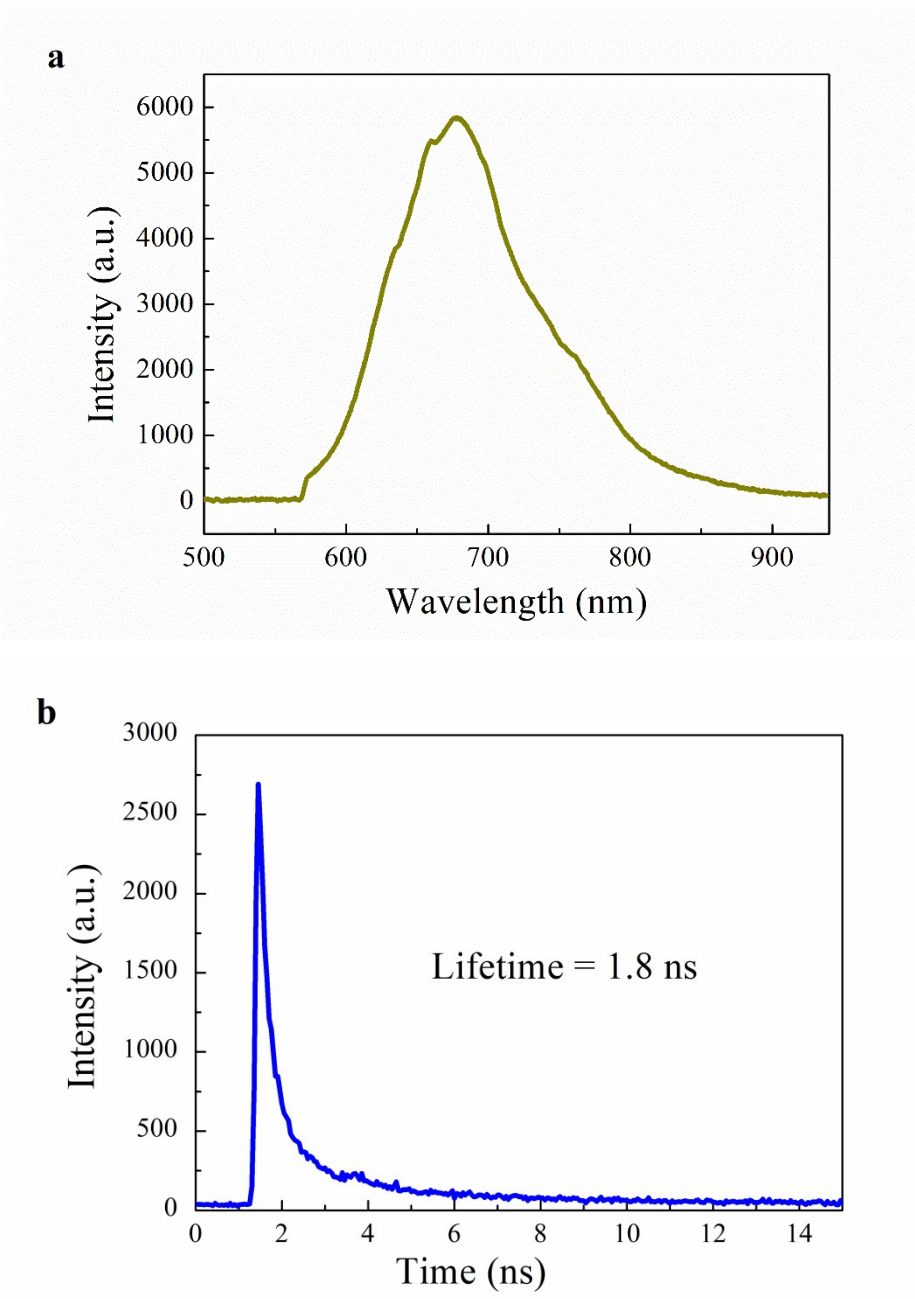

Fig. S7 (a) Photoluminescence of $Al_{2.69}B_{50}$ single crystal at room temperature. (b) Photoluminescence lifetime of $Al_{2.69}B_{50}$ single crystal.