

Band Gap of Semiconducting High Pressure Phase of Boron

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The partially ionic high pressure phase of boron γ -B₂₈ was synthesized at 12 GPa 1500°C using a multi-anvil press. The crystal structure of γ -B₂₈ was confirmed by x-ray diffraction. The γ -B₂₈ phase is metastable at ambient condition. Upon grinding, the sample back transform to α -B₁₂ phase. Optical absorption was conducted to investigate the γ -B₂₈ sample. The optical absorption edge was observed at a wavelength of 725nm indicating a band gap of 1.7 eV for this semiconducting high pressure phase, in a good agreement with theoretical calculation (1.5-1.7 eV).

Keywords: Band Gap; Semiconductor; γ -B₂₈; Boron; High Pressure.

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1. Introduction

Ever since its discovery more than two centuries ago, boron has been full of thrills and disputes for its physical and chemical properties. Located between metals and nonmetals in the periodical table, boron is considered a frustrated element. As a compromise, boron takes complex and unusual crystal structures. All boron polymorphs and even boron rich compounds consist of a B₁₂ icosahedral structure unit [1], in which each boron atom resides on a vertex of the icosahedron. Electronic properties of boron are largely determined by the intra-icosahedron and inter-icosahedron atomic interactions. Each boron atom on the vertex has five neighboring atoms within the icosahedron. However, there are only three valence electrons each of the atoms and some of these valence electrons are required for inter-icosahedron bonding. Therefore, less than three valence electrons on average are available from each of the atoms for intra-icosahedron bonding. By conventional covalent bonding, two atoms are required to form a covalent bonding based on the two-center bonding scheme in which the bonding pair of electrons resides mostly between the two bonded atoms. Thus there more required valent electrons to form two-center covalent bonding than those available within the boron icosahedron (*i.e.* electron deficiency). To account for the electron deficiency, three-center covalent bonding must be considered, for which the pair of valent electrons is shared by three boron atoms, *i.e.* the bonding pair of electrons resides in the midst of the three bonded atoms.

The electronic complexity of the icosahedral structure unit plays a critical role in leading a partial ionic bonding in the recently discovered high pressure phase γ -B₂₈ [2] While the arrangement of B₁₂ icosahedrons in γ -B₂₈ is similar to that of covalent α -B₁₂ with a slight distortion from cubic packing, all octahedral voids in γ -B₂₈ structure are occupied by B₂ dumbbells. The icosahedral and dumbbell boron atom clusters assemble into a NaCl-type structure and the different covalent bonding nature within the two clusters gives rise to charge transfer between them. In the NaCl-type arrangement, the B₁₂ icosahedra play the role of ‘anion’ while B₂ dumbbells play the role of ‘cations’. This nature makes γ -B₂₈ a boron boride, (B₂)^{δ+}(B₁₂)^{δ-}, *i.e.* a partially ionic compound, distinct from any other known form of pure boron. The charge transfer between boron atom clusters may significantly influence the electronic structure of the phase. Properties of this high pressure phase γ -B₂₈ have been studied experimentally and theoretically for its structure, mechanical properties and phase equilibrium [2-16]. Here we report result of our optical transmission spectroscopy measurement deriving the band gap of this semiconducting phase.

2. Sample Preparation

The γ -B₂₈ sample was synthesized at 12 GPa and 1500°C using a multi-anvil press a 14/8 cell assembly (an octahedral pressure medium made of MgO with 14 mm edge length inside eight WC cubes with center corners truncated down to 8 mm triangular faces). Starting material was 99.9999% chemically pure β phase of boron (B₁₀₆). A sintered BN capsule was used to contain the sample during the synthesis. The synthesized sample was examined using x-ray diffraction. Figure 1 shows the x-ray diffraction pattern of the synthesized γ -B₂₈ sample. The diffraction pattern is identical to that published earlier [2].

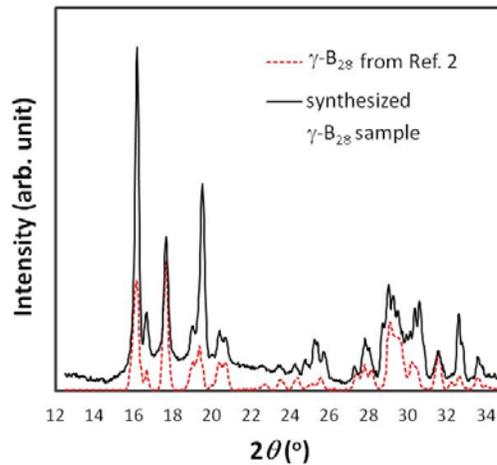


Figure 1. X-ray diffraction pattern of synthesized γ -B₂₈ sample ($\lambda = 0.7303 \text{ \AA}$). For comparison, the data from Ref. [2] is superimposed at the bottom with normalized 2θ .

The recovered γ -B₂₈ sample from high pressure is metastable at 1 atmosphere. Upon grinding, the sample is back transformed to its ambient pressure form. Figure 2 shows photos of the sample as recovered from the synthesis and during the grinding. Obvious color change is observed at the grain boundary, indicating the occurrence of back transition.



Figure 2. Optical photos of (a) synthesized γ -B₂₈ sample recovered from 12 GPa and 1500°C and (b) grinded γ -B₂₈ sample.

3. Results and Discussions

An optical band gap measurement was conducted using a FT-IR vacuum spectrometer (Bruker IFS 66v/S) and a broadband low noise light source. The sample was polished with a thickness about 10 microns. Intensities of the incident (I_0) and transmission (I_T) lights were recorded as a function of wavelength (Figure 3). The absorbance was calculated using $A = -\log(I_T/I_0)$, and plotted in Figure 3. The absorbance curve shows a clear kink at about 725nm. Beyond this wavelength, absorbance of γ -B₂₈ sample starts decreasing significantly, *i.e.* photons with lower energy than that corresponding to the wavelength of 725nm (1.7 eV) are absorbed less by the sample. This is consistent with an optical band gap of 1.7 eV in the sample. In principle, the optical band gap energy may actually be lower than electronic band gap energy for materials with a large exciton binding energy, because it is possible for a photon to have just barely enough energy to create an exciton (bound electron-hole pair), but not enough energy that can separate the electron and hole (*i.e.* the electronic band gap energy). However, in almost all inorganic semiconductors, such a difference between optical and electronic band gap energies is negligible due to very little interaction between electrons and holes.

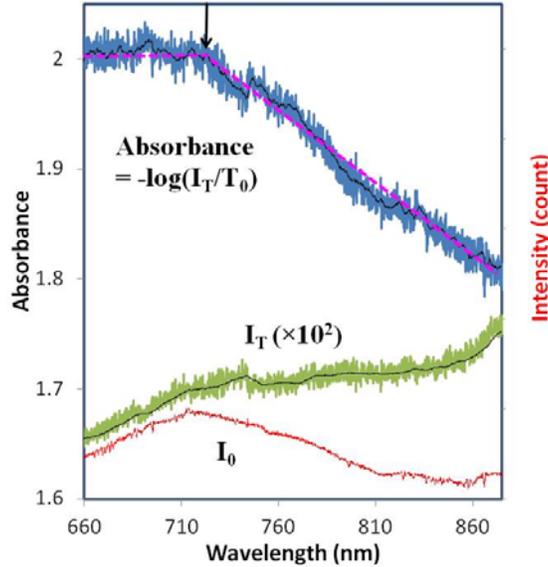


Figure 3. Measurement of optical band gap of γ -B₂₈. Incident light intensity (I_0) and transmitted light intensity (I_T) are plotted as a function of light wavelength at the bottom along the secondary axis. The derived absorbance is plotted on the top along the primary axis. The thin black lines represent moving average of the measured data. The red thick broken lines are guide for eyes to allocate the kink point (indicated by the black arrow) on the absorbance curve.

The band gap energy of 1.7 eV is very close to the earlier theoretical prediction by Oganov *et al* [2]. Their *ab initio* calculation indicates a 1.5 eV band gap at ambient pressure. Zarechnaya *et al* [5] reported a higher experimental value of the band gap energy, 2.1 eV, based on their near-infrared and optical absorption spectroscopy measurements. However, their theoretical calculation yields a band gap energy of 1.7 eV in an excellent agreement with our experimental result reported here. In another first-principles investigation of the band structure and optical properties, Xia *et al* [10] indicated that γ -B₂₈ may have an indirect band gap of 1.61 eV. The experimental and theoretical values for band gap energy of boron are summarized in Table 1.

Table 1. Table 1. Summary of theoretical and experimental results on the band gap of boron.

Phases	Band gap (eV)	Ref.
α -B12	1.6	Calc.[2]
α -B12	1.5	Calc.[12]
α -B12	1.43	Calc.[17]
α -B12	1.72	Calc.[18]
β -B106	2.0	Exp.[19]
β -B106	1.5	Exp.[20]
γ -B28	2.1	Exp.[5]
γ -B28	1.7	Calc.[5]
γ -B28	1.61	Calc.[10]
γ -B28	1.5	Calc.[2]
γ -B28	1.7	Exp. (this work)

Calc: based on theoretical calculations

Exp: based on experimental work

Although experimental result of the band gap energy of γ -B₂₈ reported here is smaller than that from the previous work by Zarechnaya *et al* [5], this value is in good agreement with all the theoretical predictions. At ambient pressure, the band gap of γ -B₂₈ is not significantly different from those of α -B₁₂ and β -B₁₀₆ whereas the feature of partially ionic bonding in γ -B₂₈ is claimed unique among all the polymorphs of boron. The theoretical calculation indicate that the band gaps for both α -B₁₂ [2, 18] and β -B₁₀₆ [18] close up at high pressure. Metallization and superconductivity has been observed in β -B₁₀₆ upon compression [21]. However, first principles calculation [2] predicted that the band gap of γ -B₂₈ is hardly influenced by pressure. Even under pressure of 200 GPa, the γ -B₂₈ phase remain s a relatively wide gap (1.25 eV). This difference in the pressure dependence of band gap may arise from the presence of charge transfer in γ -B₂₈ which results in the partially ionic bonding. Differences in equation of state and hardness between γ -B₂₈ and α -B₁₂/ β -B₁₀₆ have also been recognized in mechanical properties measurements [4,5, 7, 11, 12]. Presence of ionic bonding in γ -B₂₈ is still under debate [8]. While it is supported by *ab initio* electron energy loss near edge structure calculations [22], experimental evidence of orbital order [23] and electron-deficient [23] from high resolution single crystal diffractions, other computational work [24] remain contradictory from crystal chemistry point of view.

4. Summary

The optical band gap measurement indicates a lower band gap energy (1.7 eV) than the previously reported experimental result (2.1 eV). This is more consistent with band gap range predicted by theoretical calculations (1.5 – 1.7

eV). The high pressure γ -B₂₈ phase is wide band gap semiconductor metastable at ambient pressure.

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