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Cyclic formation of boron suboxide crystallites into star-shaped nanoplates

Sky Shumao Xie,[a,b] Hu Chen,[a] Ievgen Solodkyi,[c,d] Oleg Vasylkiv[b,d,*] and Alfred I.Y. Tok[a,*]

[a] *School of Materials Science & Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore*
[b] *Temasek Laboratories, Nanyang Technological University, 50 Nanyang Drive, 637553, Singapore*
[c] *National Technical University of Ukraine "KPI", Peremogy av. 37, Kyiv 03056, Ukraine*
[d] *National Institute for Materials Science, 1–2–1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

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Star-shaped boron suboxide (B_6O) nanoplates were formed through a liquid-phase reaction of amorphous boron and boron oxide. The formation of the five-vertex B_6O crystal is attributed to the oxygen-deficient state of B_6O_x, where $x < 1$, which correlates to the lattice parameters. The mechanical properties of spark plasma sintered B_6O show a hardness of 34.8 GPa and a fracture toughness of 4.0 MPa.m$^{1/2}$. The understanding of the relationship between crystal atomic structure and crystal morphology could be employed in the design of other boron-rich compounds.

Keywords: Boron suboxide; Powder processing; Nanostructured materials; Spark plasma sintering

Boron suboxide (B_6O) is known as a superhard material, with hardness comparable to cubic boron nitride. Since B_6O was first proved to exist half a century ago [1] it has been studied intensively, and is renowned for its extremely high hardness. One of the first studies, by Badzian [2], demonstrated the ability of B_6O to scratch the hardest (111) crystallographic plane of natural diamond. He et al. [3] reported that single-crystal B_6O had a high hardness of 45 GPa, which was comparable to that of cubic boron nitride. As well as possessing such high hardness, B_6O can be synthesized at the relatively low temperature of 1400 °C in an ambient pressure environment, making it one of the easiest superhard materials to produce, especially in comparison to diamond and cubic boron nitride. Despite the many advantages of B_6O, production of the material is still plagued by a number of problems, such as difficulty in synthesizing stoichiometrically balanced B_6O, poor crystallinity, poor sinterability and a bulk reaction product that requires further milling [3–6]. Similar to other boron-rich solids [5], many properties of B_6O remain poorly understood.

Nanocrystalline ceramics are known to possess good mechanical properties, such as enhanced super plasticity and superior strength [7]. Different nanostructural forms of B_6O have also been widely synthesized and studied by many material researchers, such as nanowires [8], nanoplatelets [9] and nanofilms [10,11]. Probably the most remarkable structure is icosahedral particles of boron suboxide. Selected area electron diffraction (SAED) patterns of these icosahedra show beautifully aligned fivefold symmetry and near-perfect icosahedral twinning [12]. Star-shaped crystals of various elements and compounds have also been observed in several studies. Example of such star-shaped crystals include ZnO, produced by chemical vapour deposition and a simple solution technique [13,14], PbS synthesized at low temperature in aqueous solution [15] and by a hydrothermal technique [16], and star-shaped gold nanoparticles [17]. The formation of two-dimensional star-shaped crystals has not observed previously.

One of the earliest mentions of star-shaped B_6O crystal formation was by Jiang et al. [8], who were studying the growth of B_6O nanowires. In their article, they suggested that cyclic twinning nanostructures were common in related boron-rich compounds. As the lattice constants of all α-rhombohedral compounds with a B_{12}-based close-packed structure change due to the different interstitial atoms, they could meet the geometric requirements for a cyclic twinning structure through the misfit stress, which is tunable through stoichiometry. In this letter, we demonstrate for the first time the synthesis of five-pointed star-shaped nanoplates

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* Corresponding authors at: School of Materials Science & Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore. Tel.: +65 91522767; fax: +65 67904935 (A.I.Y. Tok), National Institute for Materials Science, 1–2–1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. Tel.: +81 8041444747 (O. Vasylkiv); e-mail addresses: ovasylkiv@ntu.edu.sg; oleg.vasylkiv@nims.go.jp; miytok@ntu.edu.sg

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of B_6O. The super hardness of B_6O in the form of nanoplates makes it strong potential candidate in the formation of a nacre-like-structured composite material with enhanced mechanical properties. For brevity, we refer to boron suboxide nominally as B_6O, except when the stoichiometry of the compound is discussed in detail.

Boron suboxide was synthesized through a solid–liquid reaction between commercially available amorphous boron and boron oxide. The reaction process is shown in Eq. (1) below:

$$16B + B_2O_3(\text{in excess}) \rightarrow 3B_6O \tag{1}$$

Amorphous boron from Fluka (<0.1 μm, 95–97% purity) and boron oxide (B_2O_3) from Sigma–Aldrich (99.99%) were used as received. No catalyst, oxidant or reducing agent apart from the precursors was added to the reaction process. As B_2O_3 is known to undergo sublimation at 1500 °C [18], most researchers often add excess B_2O_3 in order to compensate for the B_2O_3 lost and achieve the stoichiometrically balanced B_6O [19–21]. However, in the current experiment, a copious amount of B_2O_3 was added in the molar ratio of 10:1, or 37.5% excess. As B_2O_3 forms a viscous flux above 450 °C, the excess B_2O_3 allows amorphous boron to be suspended within the viscous B_2O_3 flux throughout the reaction process. The precursors were milled using an agate mortar and pestle, with ethanol as a solvent. Subsequently, the mixed powders were loaded into a boron nitride crucible and placed in a furnace. The heat treatment process was carried out in a horizontal gas tube furnace (Elite Thermal Systems Ltd, UK) with continuous flow of inert argon gas at a maximum temperature of 1400 °C, with a holding time of 1 h.

Boron suboxide synthesized by the reaction of boron in excess B_2O_3 flux produced a transparent glassy solid embedded with fine particles of B_6O. As boron oxide dissolves fairly well in water, the solidified B_2O_3 was dissolved in an ample amount of deionized water at room temperature until all of the particles were fully dislodged from the crucible. Purification of the B_6O powder was carried out by repeated centrifugation and dilution. Filtration of the solid powder from the dissolved B_2O_3 solution was also tested and was proven to work, but resulted in the loss of powder through attachment to the filter paper. Lastly, the wet powder was placed in a drying oven at 80 °C for 12 h until the dried reddish-brown powder was collected.

X-ray diffraction (XRD) was measured using a Bruker D8 Advance diffractometer (Germany), fitted with a Cu K_α radiation source. The boron suboxide crystallographic data for refinement was based on the published XRD pattern from the Inorganic Crystal Structure Database ICSD#73624 [22]. A field-emission scanning electron microscope (FESEM; JEOL-FESEM7600, Japan) was used to study the morphology of the particles. Equipped with a thermal field emission gun, the FESEM was able to achieve a high resolution of 1.0 nm with an accelerating voltage of 15 kV. A transmission electron microscope (TEM; JEOL-TEM2010, Japan) was used to capture high-resolution images and study the crystallography of the powder. Equipped with an LaB_6 electron source and operating at 200 kV accelerating voltage, the TEM could achieve point resolution of up to 1.9 Å. Spark plasma sintering (SPS) was used to consolidate the synthesized powder using an SPS Syntex model SPS1050 (Japan). Indentation was carried out using a Vickers microhardness tester (MHV1000, China) with an applied load of 1 kg.

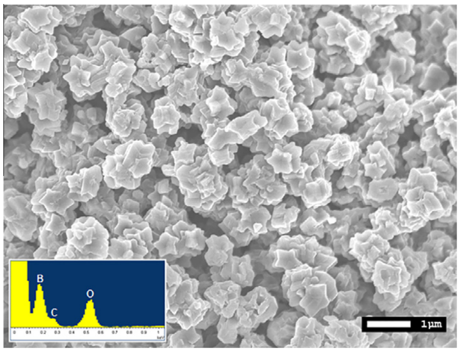

Figure 1. FESEM micrograph of synthesized sub-micron agglomerated B_6O powder with EDS analysis (inset).

The FESEM micrograph of the B_6O powder in Figure 1 shows that the dried particles were agglomerated and the particle sizes were within the sub-micron range. The agglomeration of synthesized B_6O has similarly been reported in a number of other studies [23,24]. Closer observation of the powder reveals the sharp angular edges of the particles. The energy-dispersive X-ray spectroscopy (EDS) data in the inset of Figure 1 shows strong signals at 0.18 and 0.52 keV, indicative of the presence of elemental boron and oxygen, respectively. A weaker signal at 0.27 keV was also detected, indicative of the presence of carbon – probably from the carbon mounting tape used. EDS quantitative point analysis of the star-shaped particles shows the non-stoichiometrically balanced B_6O_x, where the oxygen occupancy, x, ranges from 0.842 to 0.869. It is well known that stoichiometrically balanced B_6O can only be formed by high-pressure synthesis, whereas low-pressure synthesis typically yields an oxygen-deficient state B_6O_x, where x is less than 0.9 [3]. However, our synthesized B_6O has a relatively high content of oxygen in comparison to the pressure-less synthesis processing technique. This could be attributed to the excess B_2O_3 used, which favoured the formation of stoichiometrically balanced B_6O.

The FESEM micrograph of the powder in Figure 2(a) shows multiple five-pointed star-shaped B_6O particles orientated at different angles. It shows that the formation of star-shape particles was not an isolated phenomenon but a systematic controlled growth in a significant quantity in the powder. Figure 2(b) shows a high-magnification view of a single five-pointed star. The star-shaped surface spans a few hundred nanometres across, and the thickness is estimated to be around 40 nm. The apex angles were measured and found to range from 68.7 to 70.9°. Re-entrant angles were also measured, and were found to range from 218 to 228°. The star-shaped particle also displayed near-symmetrical fivefold rotational symmetry about its core. Rough surfaces were also observed on the star-shaped surface, characterized by nanosized bumps. The sharp angular edges of the B_6O particles endow it with strong potential for use as an effective abrasive material.

The key to understanding the star-shaped formation of B_6O lies in the study of its crystallographic properties. The crystal structure of B_6O belongs to a family of α-rhombohedral boron-rich compounds with space group $R\bar{3}m$ (No. 166). Each vertex of the rhombohedral unit cell is occupied by a single B_{12} icosahedron, which forms a rigid