Molten-salt assisted synthesis and characterization of Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers

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ABSTRACT

In this work, magnesium borate (Mg$_2$B$_2$O$_5$) and aluminum borate (Al$_{18}$B$_4$O$_{33}$) whiskers with a high aspect ratio were successfully synthesized using a molten salt method. The phase transformation and morphology involution of the whiskers were studied by XRD, IR-FT, TG-DSC, and SEM-EDS with different boron/metal ratios and reaction temperatures. The results show a rich boron environment and appropriate reaction temperature to be the crucial factors with respect to the composition and morphology of the borate whiskers. Mg$_2$B$_2$O$_5$ whiskers with a diameter of several hundred nanometers and a 10–60 length–diameter ratio were obtained when the B/Mg ratio was 1.5:1 and the reaction temperature was 800°C. For Al$_{18}$B$_4$O$_{33}$ whiskers, a synthesis temperature of 1000°C and a B/Al ratio of 3:9 were found to be optimal with respect to the whisker morphology. A liquid-solid (LS) mechanism is proposed as the growth mechanism of the whiskers on the basis of the experimental phenomena.

1. Introduction

Thanks to their excellent mechanical properties, wear resistance, low density, and thermal expansion coefficient, borate whiskers have attracted much attention in recent years, especially as mechanically strengthening materials in ceramics, metals and polymer materials [1–3]. In contrast to the high cost of the preparation process of SiC and Si$_3$N$_4$ whiskers, inexpensive raw materials and relatively moderate reaction conditions make borate-based whiskers an economical proposition [4,5]. Among these, aluminum borate (Al$_{18}$B$_4$O$_{33}$) and magnesium borate (Mg$_2$B$_2$O$_5$) whiskers in particular are attracting increasing attention due to their demonstrated unique chemical and physical properties as well as wide potential applications. For example, the properties of Al$_{18}$B$_4$O$_{33}$ whisker-reinforced aluminum and magnesium alloys are similar to those of SiC whiskers, which are widely regarded as the best type of whisker reinforcement for these composites. However, the price of Al$_{18}$B$_4$O$_{33}$ whiskers is far below that of SiC whiskers (1/10–1/30) [6–8]. Meanwhile, Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers are stable in oxidizing environments, which means they can find applications in oxidation resistant reinforcement composites, such as in the automotive, high performance defense, and aerospace fields [9].

Various methods of synthesizing borate whiskers have been developed, including combustion synthesis [10], thermal evaporation [11], sol-gel [12], chemical vapor deposition (CVD) [13], flux method [14] and the molten salt method [15,16]. A great deal of effort has been put into obtaining high-purity borate whiskers with a large aspect ratio at the lowest possible cost. For example, Elssfah et al. [17] synthesized Mg$_2$B$_2$O$_5$ single-crystalline nanorods with a uniform diameter of 70–120 nm and lengths of up to a few micrometers by directly calcining Mg(OH)$_2$ and H$_3$BO$_3$ powders without a catalyst. Peng et al. [18] obtained Al$_{18}$B$_4$O$_{33}$ whiskers by firing a mixture of Al(OH)$_3$ and H$_3$BO$_3$ with an NO catalyst. They suggested that the addition of NO accelerates the reaction between Al$_2$O$_3$ and B$_2$O$_3$ at high temperatures and increases the aspect ratio of the length to diameter of Al$_{18}$B$_4$O$_{33}$ whiskers. Wang et al. [19] synthesized Al$_4$B$_2$O$_9$/Al$_{18}$B$_4$O$_{33}$ whiskers with an average diameter distribution of approximately 400 nm and lengths ranging from 3 to 5 μm by a facile route based on the calculation of amorphous aluminum borate, which was prepared by a homogeneous precipitation reaction between aluminum isopropoxide and H$_3$BO$_3$ isopropyl alcohol solution. As described above, the composition, morphology, and crystalline phases of borate whiskers associated with their properties are highly dependent on the starting materials, synthesis, and processing methods [20]. However, many synthesis methods still produce impurities and are expensive. Meanwhile, the growth mechanism of borate whiskers remains controversial. Therefore, it is
necessary to develop new synthesis methods and to further investigate the growth mechanism of borate whiskers.

In our previous study, Al₄B₂O₉ whiskers were successfully synthesized using a wet molten salt method [21]. However, an agglomeration phenomenon and inhomogeneous size distribution appeared in the produced Al₄B₂O₉ whiskers. In this study, we report a liquid phase method and solid-phase method to synthesize Mg₂B₂O₅ and Al₁₈B₂O₃₃ whiskers, respectively. We also investigate the effect of boron/metal ratio and reaction temperature on the phase transformation and morphology evolution of these whiskers. Meanwhile, the growth mechanism of the whiskers is also proposed on the basis of the experimental phenomena.

2. Experimental

2.1. Raw materials

The raw materials used in this study include boric acid (H₃BO₃), magnesium chloride hexahydrate (MgCl₂·6H₂O), sodium hydroxide (NaOH), sodium chloride (NaCl), potassium chloride (KCl), and aluminum potassium sulfate dodecahydrate (KAl(SO₄)₂·12H₂O). All materials were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and were of analytical reagent grade.

2.2. Synthesis of Mg₂B₂O₅ whiskers

Appropriate amounts of MgCl₂·6H₂O, H₃BO₃, and NaCl were weighed and dissolved with distilled water. After they are completely dissolved, a 0.1 mol·L⁻¹ NaOH solution was added with continuous strong stirring (500 r·min⁻¹) by electromagnetic stirrer, and a large amount of white precipitate is obtained. In the reaction process, the temperature of the solution was kept at 80°C by a super-thermostatic water bath. The molar ratio of H₃BO₃, MgCl₂, NaCl, and NaOH was kept at 2:2:3:4, 3:2:3:4, or 4:2:3:4. After the reaction, the precipitate was dried in an oven, and a mixture of powders was obtained. The powders were calcined at 600–1000°C for 2 h, and then successively washed with deionized water (80°C) and ethyl alcohol to remove by-products and reduce agglomeration. Finally, the desired whiskers were obtained after drying the slurry at 80°C for 24 h. The preparation process of Mg₂B₂O₅ whiskers is shown in (Figure 1(a)).

2.3. Synthesis of Al₁₈B₂O₃₃ whiskers

Appropriate amounts of KAl(SO₄)₂·12H₂O, H₃BO₃, and KCl were weighed and thoroughly mixed and grounded in a mortar followed by drying at 120°C to remove some of the crystal water from KAl(SO₄)₂·12H₂O. The molar ratio of H₃BO₃, KAl(SO₄)₂·12H₂O, and KCl was kept at 2:9:36, 3:9:36, or 4:9:36. The arid mixture was heated to 1000°C with a heating rate of 4°C·min⁻¹ and a holding time of 1 h with an electric furnace. After cooling, the obtained powder was successively washed with deionized water (80°C) and ethyl alcohol, and then dried at 80°C. At the same time, the effects of the reaction temperature (800–1100°C) on the phase transformation and morphology evolution of the obtained whiskers were studied. The preparation process of Al₁₈B₂O₃₃ whiskers is shown in (Figure 1(b)).

2.4. Characterization

The crystallographic phases of the as-received powders were identified via X-ray diffraction (XRD, Philips PW3040/60) with copper Kα (λ = 0.154056 nm) radiation under an accelerating voltage of 40 kV. XRD was performed at a scanning rate of 5°·min⁻¹ over a 2θ range of 10° to 90° at room temperature. The Fourier-transform infrared (FT-IR) spectra of the whiskers were obtained on a Spectrum One spectrometer (Massachusetts, USA) in the 400–4000 cm⁻¹ wavenumber range. The pellets were prepared by mixing the obtained whiskers and KBr at a mass ratio of 1:500 and pressing the mixture to a disc 13 mm in diameter. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were performed on

Figure 1. Preparation process of borate whiskers: (a) Mg₂B₂O₅, (b) Al₁₈B₂O₃₃.
a thermal analyzer (SETSYS18, Setaram, France) under an air atmosphere with a heating rate of 5°C-min\(^{-1}\) over the range of 50°C to 1100°C. The morphologies of the obtained powders were observed by field emission scanning electron microscopy (FE-SEM, Zeiss–Ultra Plus, Germany) equipped with an Energy Dispersive X-ray Spectrometer (EDS).

3. Results and discussion

3.1. \(\text{Mg}_2\text{B}_2\text{O}_6\) whiskers

(Figure 2) shows XRD patterns of the powders obtained by heating the \(\text{Mg}_2\text{B}_2\text{O}_6\) precursors at 800°C for 0.2 h. It can be seen that the main phases of all three patterns were monoclinic \(\text{Mg}_2\text{B}_2\text{O}_6\), despite the molar ratio of \(\text{H}_2\text{BO}_3/\text{MgCl}_2\) (B/Mg) increasing from 1:1 to 2:1. Meanwhile, a trace of \(\text{Mg}_3\text{B}_2\text{O}_5\) phase was found in the XRD pattern when the molar ratio of B/Mg was 1:1, which was perhaps due to a small amount of \(\text{B}_2\text{O}_3\) being dismissed at high temperature. Meanwhile, the \(\text{Mg}_2\text{B}_2\text{O}_6\) phase was not found in the XRD patterns when the molar ratios of B/Mg were 1.5:1 and 2:1, which did not match the phase diagram of the \(\text{MgO-B}_2\text{O}_3\) system (Figure 3) [22]. Kitamura et al. [23] compared the reaction products of \(\text{MgO}\) and \(\text{B}_2\text{O}_3\) with and without \(\text{NaCl}\) flux. In contrast to the formation of \(\text{Mg}_2\text{B}_2\text{O}_6\) in the absence of \(\text{NaCl}\) flux, the \(\text{Mg}_2\text{B}_2\text{O}_6\) was not formed in the presence of \(\text{NaCl}\) flux at B/Mg ratios of one to four. It is suggested that the free energy of formation for \(\text{MgB}_2\text{O}_4\),

\[
\Delta G_f^\circ (\text{kJ} \cdot \text{mol}^{-1}) = -110.3 + 3419 \times 10^{-3} (T/K),
\]

has a large positive temperature coefficient and a smaller value of free energy than that of \(\text{Mg}_3\text{B}_2\text{O}_5\),

\[
\Delta G_f^\circ (\text{kJ} \cdot \text{mol}^{-1}) = -139.6 + 3.93 \times 10^{-3} (T/K).
\]

The above results suggest that the \(\text{Mg}_2\text{B}_2\text{O}_6\) phase is unstable at high temperatures and can easily be destroyed by the action of the \(\text{NaCl}\) melt. Further investigation showed that the order of \(\text{Mg}_2\text{B}_2\text{O}_6\) diffraction intensity was changed by altering the molar ratio of B/Mg. When the molar ratio was 1:1 or 2:1, the strongest characteristic peak was observed at \(2\theta = 35.06^\circ\), which corresponds to the (0, 1, 2) plane. This order of diffraction intensity was similar to that previously reported [24]. However, the strongest characteristic peak changed to \(2\theta = 31.67^\circ\) (4, 0, 2) when the molar ratio of B/Mg was 1.5:1. Meanwhile, diffractions from planes parallel to the \([0, 1, 0]\) axis, such as (2, 0, 1), (4, 0, 2), and (4, 0, 2), were relatively stronger than those of the two other patterns.

The FT-IR spectra of the obtained powders after treatment at 800°C for 2 h are reported in (Figure 4). Because no obvious peaks appeared in the range of 4000–2000 cm\(^{-1}\), only the 2000–4000 cm\(^{-1}\) range is shown in (Figure 4). It can be seen that the location and intensity of the peaks in the spectra did not

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**Figure 2.** XRD patterns of obtained powders with different molar ratios of B/Mg (a) 1:1, (b) 1.5:1, and (c) 2:1.

**Figure 3.** Phase diagram of the MgO-\(\text{B}_2\text{O}_3\) system.

**Figure 4.** FT-IR spectra of obtained powders with different molar ratios of B/Mg: (a) 1:1, (b) 1.5:1, and (c) 2:1.
significantly change when the B/Mg molar ratio increased from 1:1 to 2:1. The bands at 1495 cm\(^{-1}\) and 1297 cm\(^{-1}\) can be assigned to anti-symmetric B-O stretching vibration and the bands at 1024 cm\(^{-1}\) and 843 cm\(^{-1}\) can be assigned to symmetric B-O stretching vibration. The bands observed at 706 cm\(^{-1}\), 678 cm\(^{-1}\), and 501 cm\(^{-1}\) were due to B-O bending vibration. The band at 630 cm\(^{-1}\) is the symmetrical pulse vibration of \([\text{B}_2\text{O}_3]^+\) [25].

The morphology and nanostructure of the as-synthesized \(\text{Mg}_2\text{B}_2\text{O}_5\) powders were further characterized by SEM, and the images are shown in (Figure 5). These images suggest that the three batches of \(\text{Mg}_2\text{B}_2\text{O}_5\) powder consisted of large quantities of nanorods with uniform diameters of 200–400 nm. However, the lengths of these nanorods were different with the various of molar ratios of B/Mg. When the molar ratio was 1:1 and 2:1, the length of \(\text{Mg}_2\text{B}_2\text{O}_5\) ranged from a few hundred nanometers to more than 1000 nanometers and the length–diameter ratio was about 1–8. When the B/Mg ratio was 1.5:1, thin needle crystals of \(\text{Mg}_2\text{B}_2\text{O}_5\) were obtained as the main product, with lengths varying from a few microns to several tens of microns. The length–diameter ratio was accordingly increased to about 10–60 because the diameter was still about several hundred nanometers. Combined with the XRD results shown in (Figure 2), this suggests that the \(\text{Mg}_2\text{B}_2\text{O}_5\) whiskers were oriented in the [0, 1, 0] direction in the measurement.

In order to study the phase composition of the experiment at low temperatures, the precipitation experiment was repeated again as described in Section 2.2, except that NaCl was not added to the reaction (B/Mg = 1.5). The obtained powders were not washed with ionized water or absolute ethanol, but directly detected by XRD after drying. When the heating temperature was in the range of 80–400°C (Figure 6(a)), only the diffraction peaks of NaCl were found in the XRD patterns. The presence of this NaCl phase indicates that a reaction between \(\text{MgCl}_2\) and NaOH occurred (Eq. 1). However, the diffraction peak corresponding to \(\text{Mg(OH)}_2\) was not found in the XRD patterns. The “bread-shaped” peak appearing at about \(2\theta = 12^\circ\) (marked by the dotted frame) indicated that the generated \(\text{Mg(OH)}_2\) and \(\text{H}_3\text{BO}_3/\text{B}_2\text{O}_3\) were amorphous.

\[
\text{MgCl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Mg(OH)}_2(s) \downarrow + 2\text{NaCl}(\text{aq}) \tag{1}
\]

XRD patterns of the samples obtained by calcining the precipitate at 600–1000°C are compared in (Figure 6(b)). The main phase in the three XRD patterns was \(\text{Mg}_2\text{B}_2\text{O}_5\), despite the increase in heating temperature. However, the intensity of the diffraction peaks changed with temperatures. At 600°C, the low intensity of the diffraction peaks indicates the poor crystallization of \(\text{Mg}_2\text{B}_2\text{O}_5\). Simultaneously, the strongest diffraction peak emerged at \(2\theta = 35.14^\circ\),

![Figure 5. SEM images of \(\text{Mg}_2\text{B}_2\text{O}_5\) whiskers obtained with different molar ratios of B/Mg: (a-b) 1:1, (c-d) 1.5:1, and (e-f) 2:1.](image-url)
corresponding to the (0, 1, 2) plane. When the temperature increased to 800°C, the line width decreased while intensity of the diffraction peaks increased, demonstrating an improvement in the crystallinity of the Mg$_3$B$_2$O$_5$ whiskers. The intensity of the diffraction peak at 2θ = 31.74°, corresponding to the (−4, 0, 2) plane, was significantly stronger than that of other diffraction peaks. The XRD pattern at 1000°C was similar to that at 800°C, but the intensity of the diffraction peak at 2θ = 31.74° decreased, while the intensity of peaks at 2θ = 19.93° and 2θ = 45.11° increased.

(Figure 7) shows TG-DSC curves of the mixtures for preparing magnesium borate from 50°C up to 1000°C in an air atmosphere. Two endothermic peaks at 440°C and 801°C can be ascribed to the melting of solid B$_2$O$_3$ and NaCl, respectively. The exothermic peak at about 630°C was probably due to the contact reaction between MgO and molten B$_2$O$_3$ resulting in the formation of Mg$_3$B$_2$O$_5$.

(Figure 8) shows SEM images and EDS results for Mg$_3$B$_2$O$_5$ whiskers after heating at different temperatures for 2 h. The morphologies of the whiskers were significantly influenced by the heating temperature. At 600°C, irregular and amorphous powders (Figure 8(a)) were seen, while whiskers were not visible, which coincides with the low peak intensity of the XRD results seen in (Figure 6(b)). At 800°C, Mg$_3$B$_2$O$_5$ whiskers grow long and thin crystals with a high aspect ratio between 10 and 60. After increasing the temperature to 1000°C, the whiskers showed excessive growth (Figure 8(e)). Coarse columnar crystals of Mg$_3$B$_2$O$_5$ were obtained as the main product, with lengths varying from tens of microns to more than 100 microns, and diameters varying from a few microns to tens of microns. The aspect ratio decreased to 2–15, far lower than that of the whiskers grown at 800°C. Meanwhile, part of the crystal is presented as bulky aggregates (marked by the ellipse in Figure 8(e)). Some research shows that the mechanical properties of whiskers are closely related to their diameters. The lattice defects of the whiskers increased with increasing diameter, weakening the performance of the whiskers. These results indicate that an excessively high temperature hinders the growth of high-performance Mg$_3$B$_2$O$_5$ whiskers [24].

3.2. Al$_{18}$B$_4$O$_{33}$ whiskers

(Figure 9) shows the XRD patterns of the powders obtained by different molar ratios of B/Al. It can be seen that after being reacted at 1000°C for 1 h, the main phase of the three batches was Al$_{18}$B$_4$O$_{33}$ while no Al$_4$B$_2$O$_9$ phase was detected. Meanwhile, trace B$_2$O$_3$
and Al₂O₃ phases were detected when the molar ratio of B/Al was 4:9 and 2:9, respectively. The appearance of Al₂O₃ peaks can be explained by a local high alumina concentration that might be out of the equilibrium condition in the phase diagram of Al₂O₃-B₂O₃ (Figure 10) [25], by the slight evaporation of boron oxide [26], by stoichiometric discrepancies for the aluminum borates [27]. The most intense peak in the three batches was 2θ = 16.5°, indexed as the (1 2 0) plane of the orthorhombic Al₁₈B₄O₃₃ phase [17].

According to the phase diagram of the Al₂O₃-B₂O₃ system shown in (Figure 10), the Al₄B₂O₉ phase will appear at temperatures below 1035 °C through the reaction between liquid B₂O₃ and Al₂O₃ (Eq. 2). The Al₁₈B₄O₃₃ phase will only appear at higher temperatures when the molar ratio of B/Al exceeds 2:9 (Eqs. 3 and 4), while Al₄B₂O₉ formed at lower temperatures peritectically decomposed into Al₁₈B₄O₃₃ (Eq. 4) [28]. However, Al₁₈B₄O₃₃ was successfully synthesized at 1000°C when the molar ratio of B/Al was between 3:9 and 4:9 in this study. One possible reason is that the molten KCl added as a raw material facilitated the decomposition reaction of Al₄B₂O₉.

\[
2\text{Al}_2\text{O}_3(s) + \text{B}_2\text{O}_3(l) \rightarrow \text{Al}_4\text{B}_2\text{O}_9(s) \quad (2)
\]

\[
9\text{Al}_2\text{O}_3(s) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Al}_{18}\text{B}_4\text{O}_{33}(s) \quad (3)
\]

\[
9\text{Al}_4\text{B}_2\text{O}_9(l) \rightarrow 2\text{Al}_{18}\text{B}_4\text{O}_{33}(s) + 5\text{B}_2\text{O}_3(l) \quad (4)
\]

(Figure 11) shows SEM images of Al₁₈B₄O₃₃ whiskers with different molar ratios of B/Al. It can be seen that other than some unusual growth of Al₁₈B₄O₃₃ whiskers...
with a large diameter up to the micron level (marked by the ellipse in Figure 11), the diameter of most of the Al_{18}B_{43}O_{33} whiskers was in a uniform order of dozens to over 100 nanometers in all batches. When the B/Al ratio was 2:9, the received whiskers had a wide range of sizes with an aspect ratio of about 6–20. When the B/Al ratio increased to 3:9, more uniform and slender Al_{18}B_{43}O_{33} whiskers were obtained with diameters of dozens to more than 100 nanometers and an aspect ratio of about 8–20. However, when the molar ratio increased to 4:9, the Al_{18}B_{43}O_{33} whiskers did not become longer, instead decreasing in length. For this
ratio, the aspect ratio of the Al_{18}B_4O_{33} whiskers decreased below 10. This is potentially due to the excess boron oxide increased the resistance to alumina movement and allowed alumina to accumulate in the radial region of the whiskers, resulting in radial growth and affecting the aspect ratio of the whiskers [21].

The mixtures for preparing aluminum borate were treated in the 200–600°C range a ratio of B/Al = 3:9. The received powders were then detected by XRD without washing, and the results are shown in (Figure 12). At 200°C, KCl, KAl(SO_4)_2 · 3H_2O, and trace B_2O_3 phases were detected, which means that H_2BO_3 completely decomposed into B_2O_3 and KAl(SO_4)_2 · 12H_2O removed 9 parts of the crystal water. At 400°C, all the crystal water of KAl(SO_4)_2 · 12H_2O was removed and the KAl(SO_4)_2 phase was detected. When the temperature was further increased to 600°C, KAl(SO_4)_2 decomposed to K_2SO_4 and Al_2O_3 and SO_3 (Eq. 5), while other phases were not changed.

(Figure 13) shows XRD patterns of the samples fired in the 800–1100°C range with a ratio of B/Al = 3:9. It is difficult to distinguish the Al_{18}B_4O_{33} and Al_{18}B_4O_{33} phases due to the high similarity of their XRD patterns. The main difference was the peak at 2θ = 20.315°, belonging to the (0, 1, 1) plane, and attributable to the Al_{18}B_4O_{33} phase (marked by the dotted frame). As shown, Al_{18}B_4O_{33} (01-079-1477) was detected after low temperature thermal treatments (800°C or 900°C), while the phase changed to Al_{18}B_4O_{33} (00-032-0003) when the temperature increased to 1000°C or 1100°C. Meanwhile, no Al_2O_3 or B_2O_3 phases were detected across the whole temperature range. The transformation process of aluminum borate with temperature was similar to the results of others [19,29,30]. While no Al_4 B_2O_9 phase was detected when the temperature was 1000°C in this study, this was mainly because the transformation process of aluminum borate was promoted by using KCl molten salt as a catalyst. Clearly, the formation of Al_{18}B_4O_{33} is complete for mixtures fired at 1000°C or higher by 1 h. Seemingly, the first aluminum borate (Al_{18}B_4O_{33}) is an intermediate in the thermal evolution of the mixtures. The formation of the

![Figure 12](image1.png)

**Figure 12.** XRD patterns of raw materials after calcination at different temperatures: (a) 200°C, (b) 400°C, and (c) 600°C.

![Figure 13](image2.png)

**Figure 13.** XRD patterns of raw materials after calcination at different temperatures: (a) 800°C, (b) 900°C, (c) 1000°C, and (d) 1100°C.
intermediate is related to the viscosity of the boron-based melt; at higher temperatures, the lower viscosities would allow the dissolution and crystallization of borates during the thermal treatment.

(Figure 14) shows the TG and DSC curves of the mixtures for preparing aluminum borate whiskers across a 50–1100°C range. The TG analysis indicates that a continuous weight loss occurs across the whole temperature range. The weight loss from 50°C to about 400°C can be associated with the decomposition of H₃BO₃ and thermal dehydration of KAl(SO₄)₂·12H₂O, corresponding to the three endothermic peaks at about 80°C, 130°C, and 280°C on the DSC curve. The weight loss observed between 600°C and 1100°C is attributable to the thermal decomposition of KAl(SO₄)₂, leading to the formation of K₂SO₄, Al₂O₃, and SO₃. This weight loss corresponds to the endothermic peak at about 595°C. At the same time, the endothermic peaks at about 440°C and 670°C are attributable to the melting of B₂O₃ and K₂SO₄ with the KCl salt, respectively. The endothermic peak found at about 950°C suggests the incongruent melting of Al₄B₂O₉ into Al₁₈B₄O₃₃ and a B2O3-rich liquid (Eq. 4), which is consistent with the XRD results regarding the transformation of the aluminum borate phase (Figure 13).

(Figure 15) shows SEM images of the mixtures fired in the range of 800–1100°C. It can be seen that the whiskers obtained by firing at 800°C and 900°C shows a similar morphology, with a width of 20–50 nm and a length of 300–800 nm. When the temperature increased to 1000°C, uniform aluminum borate whiskers with a width of 50–100 μm and a length of 0.7–1.2 μm were obtained (Figure 15(c)). The morphology of aluminum borate did not significantly change after further increasing the temperature to 1100°C, except for the presence of some whiskers with an abnormal diameter. EDS microanalysis of the chemical composition demonstrated that the aluminum borate whiskers are composed of Al, B, and O. Quantitative analyses from EDS provided an approximate Al:B:O atomic ratios as shown in (Table 1), which were very close to the elemental composition in Al₁₈B₄O₃₃ (A and B points) and Al₁₈B₄O₃₃ (C and D points), respectively. The EDS results were in accordance with the XRD results shown in (Figure 13).

3.3. Growth mechanism of borate whiskers

Many mechanisms have been proposed for the growth process of whiskers in recent years, such as vapor-liquid-solid (VLS) [31], vapor-solid (VS) [32,33], self-catalytic [15,34,35], liquid-solid (LS) [36] and solid-liquid-solid (SLS) mechanisms [37]. In this study, no metal catalysts or templates were used in the raw materials, and no tips were found at the ends of the Mg₃B₂O₅ and Al₁₈B₄O₃₃ whiskers [38,39]. Meanwhile, the relatively low temperature and open environment.
chosen for our synthesis, which resulted in little B$_2$O$_3$ vapor participating in the whisker formation reaction in this study [40]. Thus, VLS and VS mechanisms were not considered to be applicable to the growth of our as-prepared Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers. Based on the characterization of the obtained whiskers, a liquid-solid (LS) mechanism (also called the dissolution-precipitation mechanism) is proposed to explain the growth of the Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers in this study.

During the preparation process of Mg$_2$B$_2$O$_5$ whiskers using the wet molten salt method, the aqueous mixture water solution of MgCl$_2$, H$_2$B$_2$O$_3$, and NaCl first reacted with NaOH solution, with the main reaction between MgCl$_2$ and NaOH generating Mg(OH)$_2$ precipitates (Eq. 4). After the reaction, the precursor mixture was dried in an oven to remove excess water. During the next heating process in the electric furnace, H$_2$B$_2$O$_3$ decomposed into B$_2$O$_3$ in the temperature range of 100–250°C (Eq. 5), and then melted at about 450°C according to the phase diagram (Eq. 6) [23]. Mg(OH)$_2$ is also decomposed into small MgO particles in this temperature range (Eq. 7). With further increasing temperature, some MgO particles started to dissolve into a molten mixture of B$_2$O$_3$ and NaCl, reacting with B$_2$O$_3$ to form Mg$_2$B$_2$O$_5$ (Eq. 8). When the generated Mg$_2$B$_2$O$_5$ exceeded the maximum melting amount in the B$_2$O$_3$ melt, Mg$_2$B$_2$O$_5$ nuclei began to precipitate and in-situ self-assembled into Mg$_2$B$_2$O$_5$ whiskers. Some research indicates that the Mg$_2$B$_2$O$_5$ phase could also form when the B/Mg ratio was in the range of 1–3 (Eq. 9), but would be unstable and decompose back into Mg$_2$B$_2$O$_5$ and B$_2$O$_3$ at the high temperatures present in the NaCl melt [23]. The addition of NaCl both acted as the medium for mass transportation and provided a uniform external environment for the growth of the Mg$_2$B$_2$O$_5$ whiskers.

$$2H_2BO_3(s) \rightarrow B_2O_3(s) + 3H_2O(g) \quad (5)$$

$$B_2O_3(s) \rightarrow B_2O_3(l) \quad (6)$$

$$2Mg(OH)_2(s) \rightarrow MgO(s) + 2H_2O(g) \quad (7)$$

$$2MgO(s) + B_2O_3(l) \rightarrow Mg_2B_2O_5(s) \quad (8)$$

$$2MgO(s) + 2B_2O_3(l) \rightarrow Mg_2B_4O_7(s) \quad (9)$$

Similar to the growth process of Mg$_2$B$_2$O$_5$ whiskers, the growth of Al$_{18}$B$_4$O$_{33}$ whiskers also included the thermal decomposition of raw materials (Eqs. 5 and 10), Al$_2$O$_3$ melts into B$_2$O$_3$ melt, a reaction between Al$_2$O$_3$ and B$_2$O$_3$ melt to form aluminum borate (Eqs. 2 and 3), precipitation of aluminum borate from B$_2$O$_3$ melt and growth of aluminum borate whiskers. From the perspective of structural chemistry, the close-packed hexagonal structure of Al$_2$O$_3$ resulted in a higher surface energy of the upper and lower sides compared with that of the surrounding six sides. Therefore, it is easier to react with B$_2$O$_3$ molecules along the [0, 0, 1] direction (Figure 8), which is the reason why the growth of Al$_{18}$B$_4$O$_{33}$ whiskers is along the c-axis [41]. Due to the small Al$_2$O$_3$ grains being well-dispersed in the molten B$_2$O$_3$ and KCl, the Al$_{18}$B$_4$O$_{33}$ whiskers can grow relatively freely and with much less agglomeration. Meanwhile, K$_2$SO$_4$ decomposing from KAl(SO$_4$)$_2$ also changed the molten state at 1000°C (Eq. 11), providing favorable conditions for Al$_{18}$B$_4$O$_{33}$ whisker growth in one dimension [17].

$$2KAl(SO_4)_{12}(s) \rightarrow Al_2O_3(s) + K_2SO_4(s) + 3SO_3(g) \quad (10)$$

$$K_2SO_4(s) \rightarrow K_2SO_4(l) \quad (11)$$

4. Conclusions

In summary, Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers with a high aspect ratio were fabricated by the molten salt method. The molar ratio of B/metal and sintering temperature had significant effects on the phase composition and morphology of these borate whiskers. Mg$_2$B$_2$O$_5$ whiskers with an aspect ratio of 10–60 were obtained when the B/Mg ratio was 1.5:1 and the reaction temperature was 800°C. For Al$_{18}$B$_4$O$_{33}$ whiskers, a synthesis temperature of 1000°C and a B/Al ratio of 3:9 were found to be the optimum conditions with respect to the whisker morphology. Under these conditions, Al$_{18}$B$_4$O$_{33}$ whiskers showed diameters in the nanometer range and an aspect ratio of 8–20. The growth of Mg$_2$B$_2$O$_5$ and Al$_{18}$B$_4$O$_{33}$ whiskers followed the liquid-solid (LS) mechanism.

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Disclosure statement

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