Chemical Preparation of Aluminum Borate Whiskers

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Aluminum borate ($9Al_2O_3{\cdot}2B_2O_3$) whiskers were chemically synthesized in potassium sulphate flux by using the starting chemicals of aluminum sulphate and boric acid. The synthesis temperature of 1075°C was found to be the optimum with respect to whisker morphology. A tentative XRD pattern was suggested for the whiskers produced after heating at 1150°C. The product purity, phase composition, and whisker morphology were investigated by XRD, EDXS, and SEM, respectively.

Introduction

$9Al_2O_3{\cdot}2B_2O_3$ is a compound with a melting point of 1440°C [1]. It has a low density, 2.93 g/cm3 [1], and a low coefficient of thermal expansion [2]. It tends to form needle-shaped crystals [3]. These characteristics suggest that $9Al_2O_3{\cdot}2B_2O_3$ could be an alternative material for whiskers to reinforce light metals like aluminum alloys [4]. Whiskers of $9Al_2O_3.2B_2O_3$ have been synthesized [5] by a vapor phase method, by solid-state reactive firing [6-10], and by a flux method using borates [11, 12]. However, the product yields were found to be very low, 10% or less. The low yields in the flux method were attributed to glass forming between the flux and aluminum compounds [3, 11, 12].

Aluminum borate whiskers have been synthesized by a Japanese chemical company (Shikoku Chemical Co. Ltd.) in cooperation with the Government Industrial Research Institute of Shikoku since April 1989 and is commercially available from the above-mentioned company, under the trade name of ALBOREX [4]. The low price of the whisker is one of the incentives to adopt these whiskers for use in metal matrix composites in industrial uses, such as automobile engine components, heat insulating materials, and filter media [4, 13].

The present study attempts to determine the experimental parameters and conditions of the synthesis of $9Al_2O_3{\cdot}2B_2O_3$ whiskers by first mixing the water-soluble starting materials in de-ionized water, as compared to conventional ball-milling of the chemical powders. The starting point for this work has been chosen as the experimental synthesis parameters described by Wada *et al*. [3, 11, 12].

Experimental

Aluminum sulphate ($Al_2(SO_4)_3.18H_2O$, 99.9%, Riedel de-Haen, Seelze, Germany), boric acid (H_3BO_3: 99.9%, Riedel de-Haen, Germany) and potassium sulphate (K_2SO_4: 99.9%, Merck, Darmstadt, Germany) were accurately weighed in proper amounts to give the following atomic ratios: B/Al = 2/8, 3/7, and 4/6, in separate batches of these starting materials. Potassium sulphate (m.p.: ~1070°C) is used as the fluxing agent in this process. The ratio of (K_2SO_4/B+Al) was kept constant at 10/10 throughout this study.

The starting materials used were all soluble in water. These substances were first dissolved in 200 mL of de-ionized water, in a 400 mL-capacity glass beaker, in the order given above. The solution was then heated to about 95°C on an hot-plate and stirred with the aid of a magnetic stirrer. Following the dissolution of the starting materials, the clear solution was completely evaporated to dryness. The clear, glassy residue in the beaker was dried overnight in an oven at 100°C. Solid residue was then ground by an agate mortar and pestle into a fine powder.

The homogeneous powder mixtures of the initial starting materials were placed (as a loose powder) in clean alumina crucibles. The synthesis temperatures of 1075° and 1150°C were studied in this work. The soaking time (at the peak temperature in a stagnant air atmosphere) was kept constant at 3 hours. The samples were heated from the ambient to the peak temperature of whisker synthesis at a heating rate of about 4°C/min. Following the constant soaking of 3 hours at the peak temperatures, the samples were cooled naturally to room temperature within the shut-off furnace.

The white solid residues were then gently scraped off of the alumina crucibles, and (without grinding) were placed in a 100 mL of 50 vol% HCl solution to wash out the fluxing agent, i.e., K_2SO_4. The solid product was washed in stirred HCl solutions (at 85-90°C) for 90 minutes. The yellowish mother liquor was then filtered out, and the filtrate on the filter paper was washed several times with de-ionized water for neutralization. The wet cake of whisker body was finally dried overnight in an oven at 100°C. The liquors after acid-wash have been examined for the metal cation concentrations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin Elmer, Model: Plasma-1000, UK).

Phase purity and chemical composition of the produced whiskers were investigated by powder X-ray diffraction (XRD: Rigaku, DMax/B, Tokyo, Japan) and by energy dispersive X-ray spectroscopy (EDXS: Kevex, CA, USA). Further details of XRD work are given in Table 1.

Table 1. Powder Diffraction Data for Phase Characterization

Radiation type, source	: X-rays, Fe or Cu, 40kV, 20 mA
Wavelength used	: 1.9360 (or 1.5406) Å $K_{\alpha 1}$, monochromatic
λ Discrim.	: Diffracted beam, graphite-mono
λ Detector	: Scintillation
Instrument description	: Div.: 1° Rec.: 0.3°
Instrumental profile breadth	: 0.10°2θ
Temperature (°C)	: 22 ± 2
Range of 2θ from	: 10 to 90°
Specimen form	: Side-loaded powder, packed for 2θ's
Specimen motion	: None
Step size	: 0.02° 2θ
Count time	: 5 s
External 2θ standard	: Si (Starck Co., Germany)
Lattice parameter of 2θ standard	: 5.4310 Å
2θ error correction procedure: Linear interpolation from nearest 2θ's of std.	
Intensity meas. technique	: Peak heights, automated computer software (Rigaku, DMAX-B) and "Peakfit 3.0" (Jandel Scientific, USA)
Peak heights Error	: ~ 5%
Cell refinement method	: Least-squares, Appleman & Evans (1973).

Morphology of the synthesized whiskers was examined by scanning electron microscopy (SEM: JEOL, Model: JSM-6400, Tokyo, Japan). The samples for SEM and EDXS investigations were, first, sputter coated with an approximately 25 nm-thick layer of a gold-palladium alloy. EDXS analyses were carried out on the samples to perform a semi-quantitative analysis for the determination of the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to about ± 3 wt%.

Results and Discussion

The compositions/heating temperatures studied, and the resultant phase constitutions of the whisker synthesis experiments are summarized in Table 2. The ratio of (K_2SO_4/B+Al) was kept constant at 10/10. The heating times at the peak temperatures were 3 hours for all samples.

Table 2. Phase constitution of samples produced during aluminum borate whisker synthesis

Temperature (°C)	**Atomic B/Al ratio**		
	2/8	**3/7**	**4/6**
1075	$9Al_2O_3{\cdot}2B_2O_3$	$9Al_2O_3{\cdot}2B_2O_3$	$9Al_2O_3{\cdot}2B_2O_3$
1150	$9Al_2O_3{\cdot}2B_2O_3$	$9Al_2O_3{\cdot}2B_2O_3$	$9Al_2O_3{\cdot}2B_2O_3$

ICP-AES measurements in the potassium sulphate liquors (after acid-washing) indicated only the trace (< 30 ppm) presence of Al + B. This meant that during the acid-wash step the whiskers retained their chemical composition and did not decompose. It was found by powder XRD and EDXS runs that, at all compositions investigated, the final product was phase-pure $9Al_2O_3{\cdot}2B_2O_3$. The semi-quantitative EDXS measurements (30-points analyses on each sample) yielded the constant Al/B atomic ratio of 4.51 ± 0.2 (i.e., 86 wt% Al_2O_3) for all the powder samples of Table 2. The chemical composition of these whiskers can best be described by the formula of $9Al_2O_3.2B_2O_3$.

Belov, *et al*. [14] synthesized crystals of $Al_5(BO_3)O_6$ from a melt of Y_2O_3-MoO_3-K_2O-Al_2O_3-B_2O_3. Although the chemical analysis of these crystals were reported as 86 wt% Al_2O_3 (i.e., $9Al_2O_3{\cdot}2B_2O_3$), they assigned the chemical formula of $10Al_2O_3{\cdot}2B_2O_3$ (i.e., 88 wt% Al_2O_3) with the space group of *Cmcm*, in accord with their further structural interpretation of this phase. Ihara, *et al*. [15] determined the crystal structure of $9Al_2O_3{\cdot}2B_2O_3$ by single-crystal XRD analysis. They found that the structure was a $10Al_2O_3{\cdot}2B_2O_3$-type and contained AlO_6 octahedra, AlO_4 tetrahedra, B_2O_3 triangles, and five oxygen-coordinated aluminum atoms. Their analyses suggested that the structure was a deficient one as described by Scholze [1], but less than 2% of the aluminum atom positions were occupied by boron atoms. Schneider, *et al*. [6], on the other hand, preferred the chemical formula of $9Al_2O_3{\cdot}2B_2O_3$ (with the space group of $A2_1\,am$) to designate this phase in their relatively recent crystallographic study.

The synthesized whiskers of aluminum borate of this study were found to be orthorhombic with the following experimental lattice parameters; a = 15.0077, b = 7.6850, c = 5.3088 Å, and V = 612.29 $Å^3$. This orthorhombic structure possessed the space group of *Amam (63)*. This assignment of the space group is in coincidence with the previous work of Schneider, *et al.* [6].

The XRD patterns of our experimental samples were believed to display better crystallographic quality than that of the ICDD PDF 32-3 already present for this phase. A tentative, new XRD pattern for $9Al_2O_3 \cdot 2B_2O_3$ whiskers formed from a "2 / 8" (B/Al ratio) batch is presented in Table 3.

Table 3. Powder diffraction data for $9Al_2O_3 \cdot 2B_2O_3$ synthesized at 1150°C

$2\theta_{exp}$ (°)	I/I_o	d_{exp} (Å)	h k l	$\Delta 2\theta^*$ (°)
11.783	2	7.5044	2 0 0	-0.001
16.496	100	5.3696	2 1 0	-0.002
20.315	23	4.3680	0 1 1	0.000
23.129	6	3.8424	0 2 0	0.000
23.693	8	3.7522	4 0 0	-0.002
26.029	10	3.4206	2 2 0	-0.003
26.414	33	3.3716	4 1 0	0.000
31.403	4	2.8464	4 1 1	-0.003
33.348	33	2.6847	4 2 0	-0.003
35.853	12	2.5026	2 0 2	-0.002
37.050	3	2.4245	2 3 0	-0.003
39.009	3	2.3071	0 3 1	0.000
39.492	7	2.2800	3 3 0	+0.002
41.309	14	2.1838	0 2 2	+0.003
41.646	4	2.1669	4 0 2	0.000
42.703	16	2.1157	4 3 0	-0.002
43.144	3	2.0951	3 3 1	-0.002
45.265	1	2.0017	3 2 2	-0.004
46.573	3	1.9485	5 3 0	0.000
47.275	2	1.9212	0 4 0	+0.002
48.483	3	1.8761	8 0 0	-0.004
48.891	3	1.8614	2 4 0	-0.005
50.008	7	1.8224	8 1 0	+0.001
50.990	2	1.7896	6 3 0	+0.001
51.546	3	1.7716	6 1 2	-0.006
53.065	1	1.7244	0 1 3	-0.007
53.534	4	1.7104	4 4 0	-0.011
54.379	9	1.6858	8 2 0	0.000
57.637	4	1.5980	1 2 3	+0.008
58.897	4	1.5668	4 1 3	+0.004
59.334	2	1.5563	0 4 2	+0.003
60.363	1	1.5322	8 0 2	-0.009
61.193	12	1.5134	8 3 0	+0.006
62.903	2	1.4763	0 5 1	+0.003
63.464	2	1.4646	6 4 1	-0.003
64.223	4	1.4491	1 3 3	+0.004
65.860	5	1.4170	5 2 3	-0.002
66.877	2	1.3979	10 2 0	+0.002
68.533	1	1.3681	5 5 0	-0.002
69.155	2	1.3573	4 3 3	+0.003
70.034	2	1.3424	8 4 0	-0.011
70.950	6	1.3273	0 0 4	-0.006
72.262	4	1.3064	10 0 2	+0.001
73.013	1	1.2948	10 3 0	+0.007
73.943	1	1.2808	0 6 0	+0.002

74.589	1	1.2713	6	5	1	+0.008
75.192	1	1.2626	2	6	0	-0.002
75.827	5	1.2536	4	5	2	+0.004
77.185	2	1.2349	4	1	4	+0.005
77.572	1	1.2297	4	4	3	+0.001
77.669	1	1.2284	2	6	1	-0.007
77.910	1	1.2252	9	4	1	+0.010
78.621	1	1.2159	7	5	1	+0.004
80.760	1	1.1890	8	5	0	-0.007
81.673	2	1.1780	5	6	0	+0.005
83.794	1	1.1535	0	6	2	+0.005
84.999	1	1.1402	2	6	2	-0.003
87.425	1	1.1147	6	6	1	-0.005
89.724	2	1.0920	0	4	4	-0.002

* $2\theta_{exp} - 2\theta_{calc}$

The experimental XRD pattern for the single-phase $9Al_2O_3 \cdot 2B_2O_3$ sample of Table 3 was given in Figure 1.

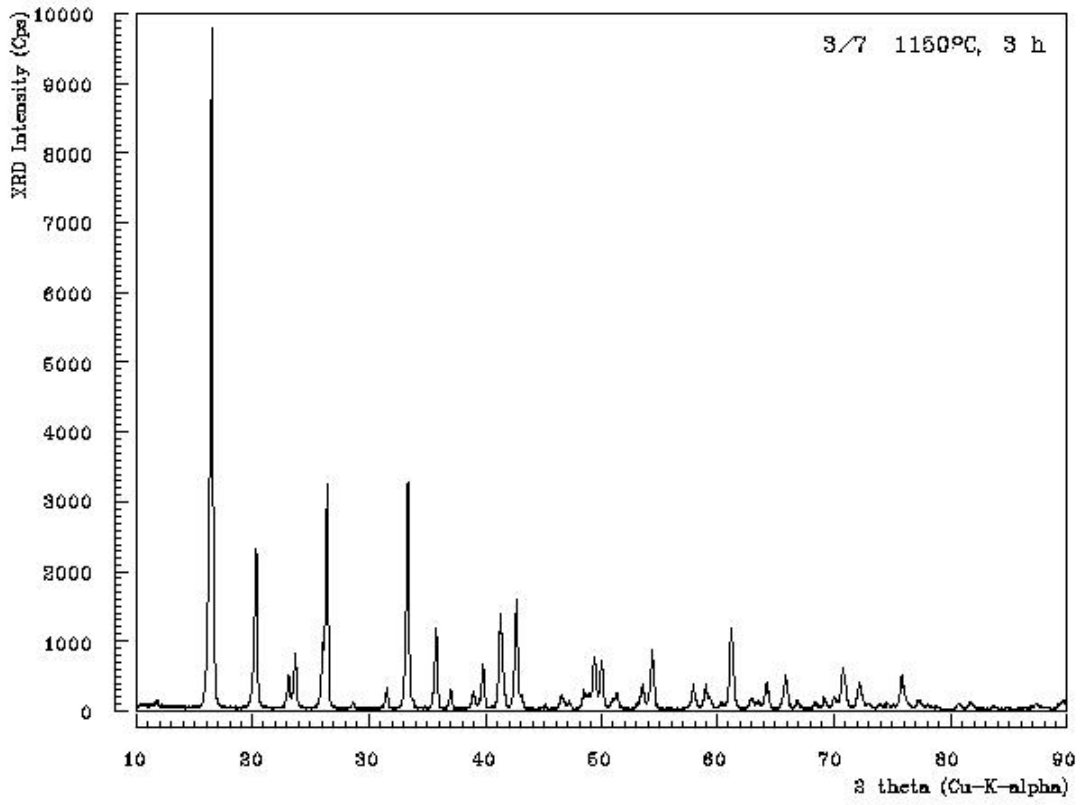

Figure 1 Experimental XRD pattern of $9Al_2O_3 \cdot 2B_2O_3$ whiskers of Table 3 synthesized at 1150°C

Figure 2 shows the typical XRD spectra of the whiskers synthesized at the peak temperature of 1075°C for the three B/Al ratios studied. The Miller indices of the orthorhombic unit cell of $9Al_2O_3 \cdot 2B_2O_3$ were labelled on top of each reflection. It was also confirmed by the semi-quantitative EDXS runs performed on these samples that the synthesized whiskers had the stoichiometric B/Al ratio of 2/9, and they were free of any potassium impurity which would originate from the fluxing agent used. This fact also proved the high-levels of efficacy achieved in the HCl washing step.

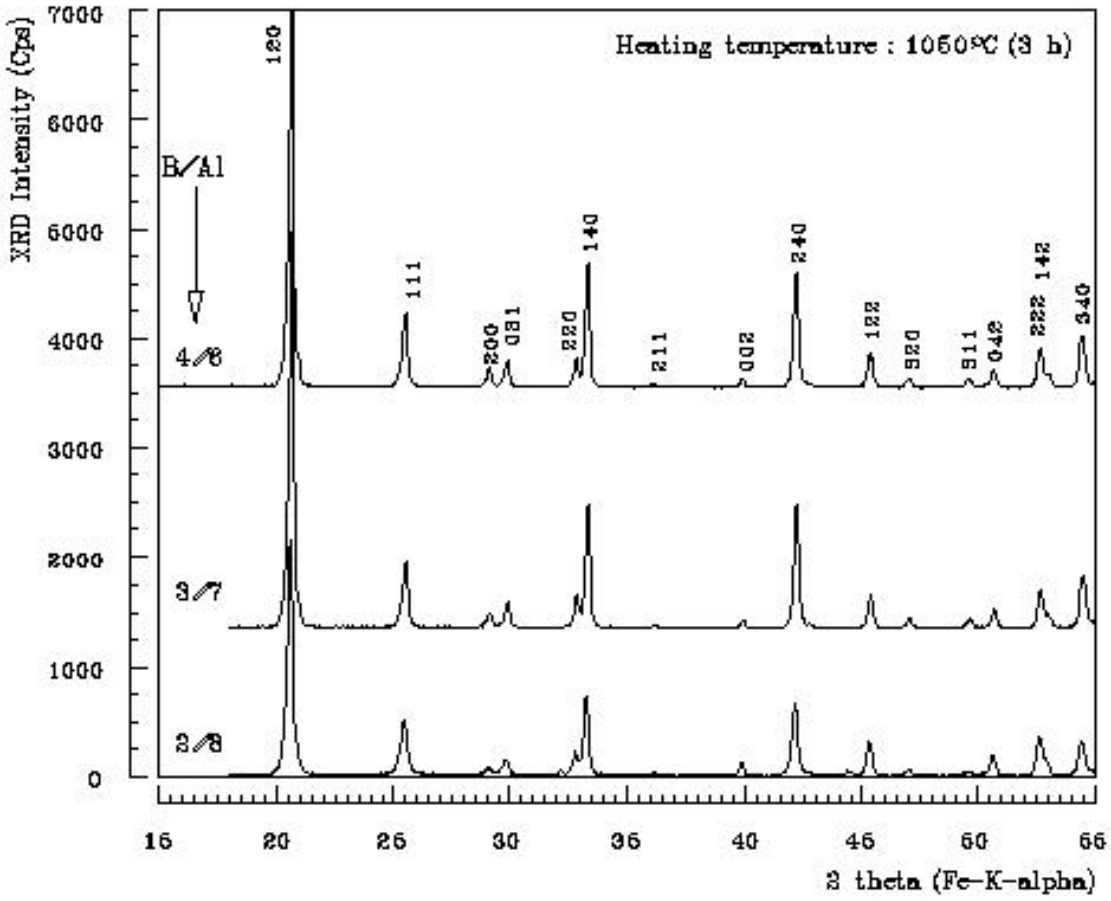

Figure 2 XRD spectra of whiskers synthesized by using different B/Al ratios in the starting batch

The morphology of the whiskers synthesized in this study was investigated by the SEM micrographs taken from each sample. Figure 3 shows the whiskers obtained at different B/Al ratios, at the constant temperature of 1075°C. The sub-micron-thick (about 250 nm) whiskers shown were randomly-oriented, interlocked and a few tens of microns long. The increased peak soaking temperature, from 1075° to 1150°C slightly altered the orientation of the whiskers. There was also some diminutive evidence from the SEM studies that increasing temperature would also slightly increase the whisker thickness. The reaction sequence during the synthesis of aluminum borate whiskers has been previously described by Wada, *et al*. [11].

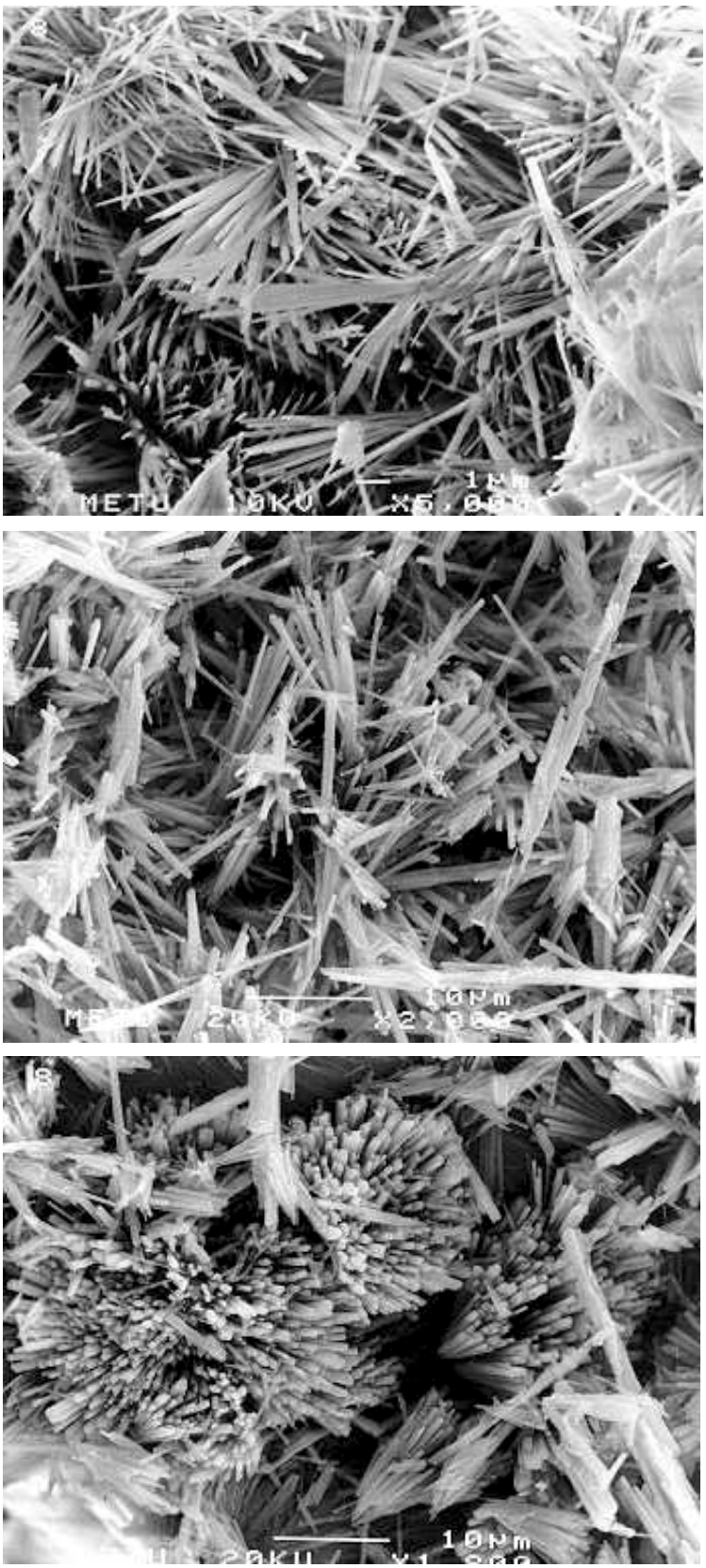

Figure 3 SEM micrographs of whiskers synthesized at 1075°C; B/Al ratios: (*top*) 2/8, (*middle*) 3/7, (*bottom*) 4/6

Summary

$9Al_2O_3{\cdot}2B_2O_3$ whiskers (86 wt% Al_2O_3), of superior mechanical properties (previously reported), were synthesized by using a flux-growth method from the starting materials of high-purity aluminum sulphate, boric acid, and potassium sulphate. The dissolved starting materials were evaporated to dryness during powder batch preparation. Three different B/Al ratios and two synthesis temperatures were investigated for their influence on the phase constitution of whiskers. All of the composition-temperature combinations studied in this work yielded single-phase $9Al_2O_3{\cdot}2B_2O_3$. A tentative XRD pattern for $9Al_2O_3{\cdot}2B_2O_3$ has been suggested to replace the present card for that phase in the ICDD-PDF database.

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