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Preparation of Aluminum Borate ($Al_4B_2O_9$) Nanowires by Borax

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Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] and sodium borate [$Na_2B_4O_7 \cdot 10H_2O$] powders were used as starting materials, chiral (L- or D-) tartaric acid was added to serve as dispersing agent, a sol-gel process followed by annealing was employed to fabricate single crystal aluminum borate ($Al_4B_2O_9$) nanowires. the S-types curve of pH value of the solution system under certain ratio of Al/B was to be nominated and to be promising in a large-scale production of aluminum borate ($Al_4B_2O_9$) nanowires.

Keywords: Aluminum borate, Nanowires, Scale-up, Sol-gel, Chiral tartaric acid.

INTRODUCTION

Aluminum borate are remarkable ceramic materials with high elastic modulus and tensile strength, excellent resistance to corrosion and thermal properties attractive for structure applications, optical electronics and tribology. Especially the aluminum borate whiskers have great potential in oxidation-resistant, reinforced composite[1].

As we know aluminum borate nanowires including $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$, the $Al_{18}B_4O_{33}$ nanowires have higher hardness and elastic modulus than $Al_4B_2O_9$ nanowires contributed to the improvement of the mechanical properties. Aluminum borate ($Al_{18}B_4O_{33}$) whisker-Mg, Al and their alloy reinforced composite can be made from modification by coating with Cr_2O_3, ZnO, SnO_2, *etc.*[2-8], aluminum borate ($Al_{18}B_4O_{33}$) whisker/x (aluminum phosphates, epoxy phenolic paint, PMMA, ABS glass, *etc.*) reinforced composites[9,10-13] may be used as wave-transparent materials, reinforced coating and electroless coating. The aluminum borate whisker can also provide aqueous solution with good friction reduction and anti-wear properties[14]. Recently agrobacterium-mediated transformation of kabocha squash induced by wounding with aluminum borate whiskers ($Al_{18}B_4O_{33}$) have been discovered[15]. The discovery opens a new application fields in plants so much as biology except mechanical and thermal properties. Simultaneously study on the type of crystallites ($Al_4B_2O_9$ and $Al_{18}B_4O_{33}$) need recognition again rather than detail study on ($Al_{18}B_4O_{33}$).

The amount and type of crystallites ($Al_4B_2O_9$ and $Al_{18}B_4O_{33}$) formed depended on the heat treatment temperature, starting materials and method[16-19]. Aluminum borate nano-particles with diameter of 30-50 nm can be obtained by the way of direct deposition[14]. Aluminum borate nanorods obtained by sol-gel method[20], a low-heating-temperature(750 °C) solid-state precursor method[21] and an ammonium bromide (CTAB)-assisted sol-gel method[22]. Aluminum borate nanowies can be obtained by a chemical reaction with a supported catalyst[23], by firing a powder compact[24], *via* a novel flux method[25], by a solid-state reaction[26]. ($Al_4B_2O_9$ and $Al_{18}B_4O_{33}$) nanowires can be obtained by a sol-gel process followed by annealing[16], by one-step combustion method[17] and *via* a precipitation process[19]. $Al_{18}B_4O_{33}$ microtubes can be obtained by an aqueous method[1]. The aluminum borate ($Al_{18}B_4O_{33}$, $Al_4B_2O_9$) nanowires and nanotubes can be concurrently obtained by a chemical vapor deposition (CVD) method[18]. The polyol including citric acid and lactic acid[16,17] were used usually as dispersing agent which plays an important role on the synthesis of aluminum borate nanowires and chiral (L-, or D-) polyol were rarely reported to be used.

The content of boron oxide in $Al_4B_2O_9$ was obviously more than $Al_{18}B_4O_{33}$, the boron oxide is one of the important plant microelements and its auxo-action on plant growth have been testified[27], relatively low temperature required to obtained the type of crystallites ($Al_4B_2O_9$) and the $Al_4B_2O_9$ nanowires have better crystallinity than the $Al_{18}B_4O_{33}$ nanowires, and the structure characterization indicates that the $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$ nanowires have different growth behaviour.

The study on the type of crystallites ($Al_4B_2O_9$) is rarely and on its application is still none reported. These indicate in synthesizing and probing potential applications of aluminum borate ($Al_4B_2O_9$) nanowires. In our present work, aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) powders were used as starting materials and dispersed by L-, or D- tartaric acid to product aluminum borate ($Al_4B_2O_9$)

nanowires by a sol-gel process followed by annealing. The S-types curve of pH value of the solution system was to be nominated and to be promising in a large-scale production of aluminum borate ($Al_4B_2O_9$) nanowires.

EXPERIMENTAL

Aluminum nitrate [$Al(NO_3)_3·9H_2O$] and sodium borate ($Na_2B_4O_7·10H_2O$) powders were used as starting materials, L- or D-Tartaric acid was added to serve as dispersing agent. Aluminum nitrate [$Al(NO_3)_3·9H_2O$], sodium borate ($Na_2B_4O_7·10H_2O$) and citric acid, tartaric acid, L- or D-tartaric acid and lactic acid were dissolved in deionized water, respectively. Mix the aqueous solution of aluminum nitrate (0.167 M, 250 mL) and L- or D-tartaric acid aqueous solution together, subsequently, sodium borate ($Na_2B_4O_7·10H_2O$) aqueous solution (0.167 M, 250 mL) were added dropwise (4-5 s/drop) to the above mixed aqueous solution. The solution was maintained under constant stirring (300 rpm) with a mechanical stirrer, reaction temperature at 53 °C and reaction time 4 h. The mixture solution were gelling with 12 h, the precipitate was washed first with deionized water and then methanol several times and dried at 80 °C for 12 h. The obtained gels were put in crucibles and then annealed in a muffle furnace at 950 °C for 2 h under ambient atmosphere. The white powder obtained were washed by deionized water and methanol 3 times repeatedly and dried at 80 °C in air.

The pH value of the reaction process were monitored by pH acidimeter (PHS-3C), the obtained products were characterized by X-ray diffractometer (XRD, D/max-rA, with CuKα radiation) and scanning electro-microscopy (SEM), the transmission electron microscopy (TEM) observation was carried out using a JEM-3000F(JEOL).

RESULTS AND DISCUSSION

Sodium borate ($Na_2B_4O_7·10H_2O$) is strong alkali and weak acid salt, $Al(OH)_3$ precipitation produced when the pH value of the solution reached the limited solubility constant. The change interval of pH value of $Al(OH)_3$ precipitation in the aqueous solution was 3.2-4.8 according to the calculation of the solubility constant. Fig. 1 shows the monitored change of pH value of the reaction process under certain ratio of Al/B. The change interval of pH value of $Al(OH)_3$ precipitation in the aqueous solution was 3.2-4.8 have been recorded in the S-type curve. Maintain one curtained pH value of the aqueous solution was the control point for production of aluminum borate nanowires other than $Al(OH)_3$ precipitation.

Fig. 2 shows the SEM of aluminum borate nanowires with the change of pH value of aqueous solution between 3.3-3.9 under citric acid as dispersing agent. The amount and type of the aluminum borate nanowires are relatively pure and uniform in Fig. 2a and 2b as the pH value of aqueous solution located at 3.3 and 3.5 and a few agglomeration appeared in Fig. 2c and d as the pH value of aqueous solution located at 3.7 and 3.9. Aluminium(III) in the aqueous solution exist a transformation from hydroxyl polymer to indeterminate form[28] and same phenomenon taken place in the mixture solution, the indeterminate form even precipitate of $Al(OH)_3$ generate with the increase of pH value or content of OH^-. This is the reason that a few agglomeration in the SEM of aluminum borate nanowires appeared.

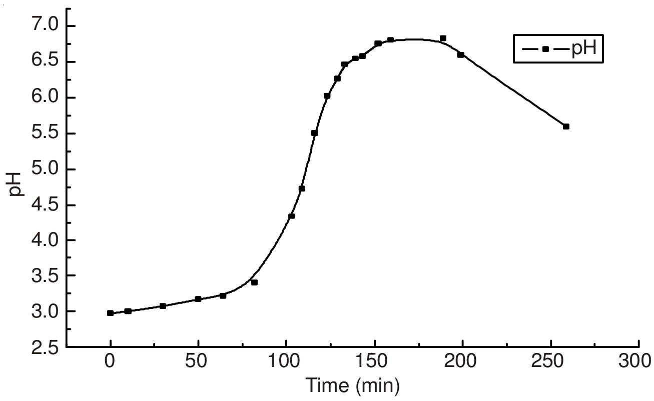

Fig. 1. Change of pH value with reaction process under certain ratio of Al/B

The XRD pattern of the product with calcining temperature of 900 °C for 2 h were shown in Fig. 3, it was clearly seen that the fitting crystalling parameters are a = 14.74 Å, b = 15.26 Å and c = 5.557 Å (JCPDS-ISD, PDF#29-0010) was the only phase of aluminum borate ($Al_4B_2O_9$) while the pH value of the solution system are 3.5 and 3.7, but the peak of a small number of Al_2O_3 arise as the pH value of the solution system are 3.7 then 3.5.

The annealing temperature were setup at 850, 900 and 950 °C. The SEM observation results on the products were shown in Fig. 4e, f and g. The minimum temperature required

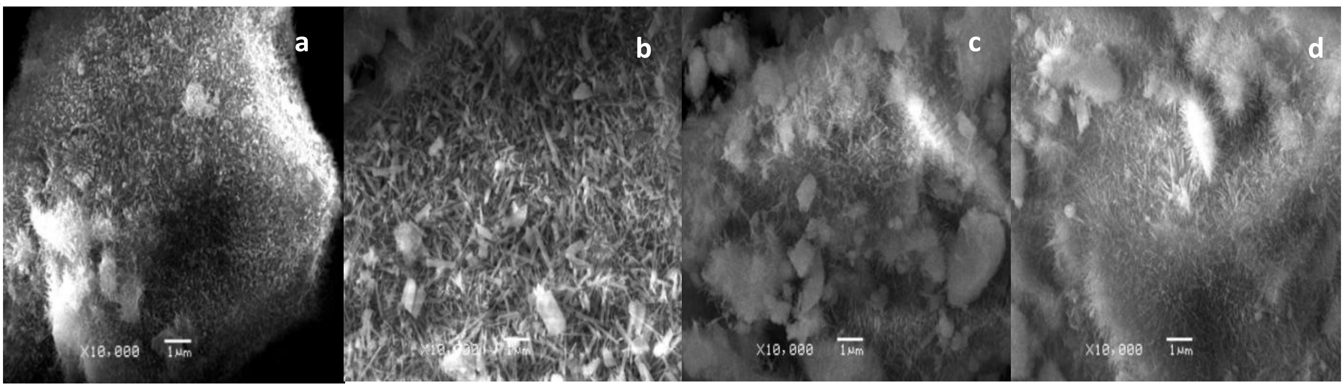

Fig. 2. SEM of aluminum borate nanowires with the change of pH value (a = 3.3, b = 3.5, c = 3.7, d = 3.9)

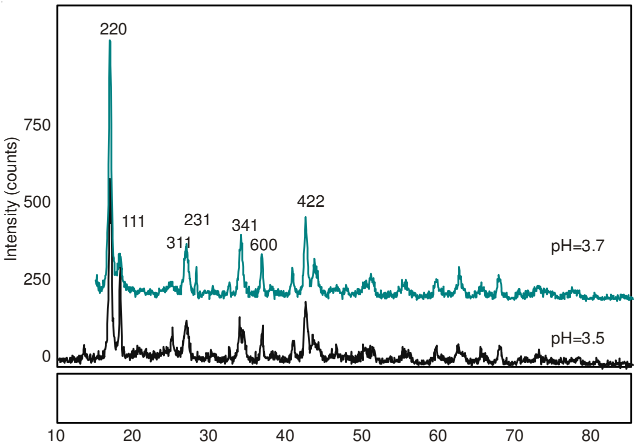

Fig. 3. XRD pattern of the product with calcining temperature of 900 °C

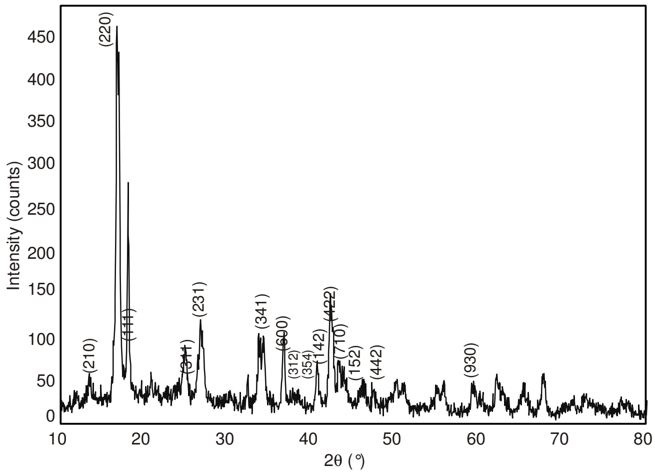

Fig. 5. XRD pattern of the product with calcining temperature (K = 950 °C)

for the formation of $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$ nanowires are 780 and 1020 °C, respectively, meanwhile, the phase transforma tion from $Al_4B_2O_9$ to $Al_{18}B_4O_{33}$ over 1020 °C corresponded to previous report[17]. The morphology and the dispersibility of the aluminum borate nanowires were uniform, extra low impurity appeared and the mean diameter were 70 nm under annealing temperature were setup at 950 °C.

The XRD pattern (Fig. 5) of the product identified the formation of an aluminum borate ($Al_4B_2O_9$) nanowires at 950 °C, $Al_4B_2O_9$, the fitting crystalling parameters are a = 14.74 Å, b = 15.26 Å and c = 5.557 Å (JCPDS-ISD, PDF#29-0010) was the only phase and a few $Al_{18}B_4O_{33}$, the fitting crystalline parameters are (JCPDS-ICSD, PDF#29-0009) was also present, in accordance with the phase diagram actually, the $Al_{18}B_4O_{33}$ phase is expected to form at about 1040 °C by the decomposition of $Al_4B_2O_9$[17].

Fig. 6 shows the SEM observation results on the products as the citric acid, tartaric acid, L-tartaric acid and D-tartaric acid were used as dispersing agent under the pH value of aqueous solution located at 3.5. The results indicated that the effect of the tartaric acid used as dispersing agent was the worst and the L-tartaric acid and D-tartaric acid were better than citric acid as dispersing agent relatively.

The XRD pattern (Fig. 7) of the product identified the formation of an aluminum borate ($Al_4B_2O_9$) nanowires at 900 °C for 2 h while the citric acid, tartaric acid, L-tartaric acid, D-tartaric acid and lactic acid were used as dispersing agent, the fitting crystalling parameters *i.e.*, a = 14.74 Å, b = 15.26 Å and c = 5.557 A (JCPDS-ISD, PDF#29-0010) was the only phase of aluminum borate ($Al_4B_2O_9$). It was seen that inductive effect were very good as L-tartaric acid as citaric acid were used in dispersing phenomena.

Fig. 8 m and n shows the SEM results on the products and the TEM image of a typical fiber of the ten times scale-up

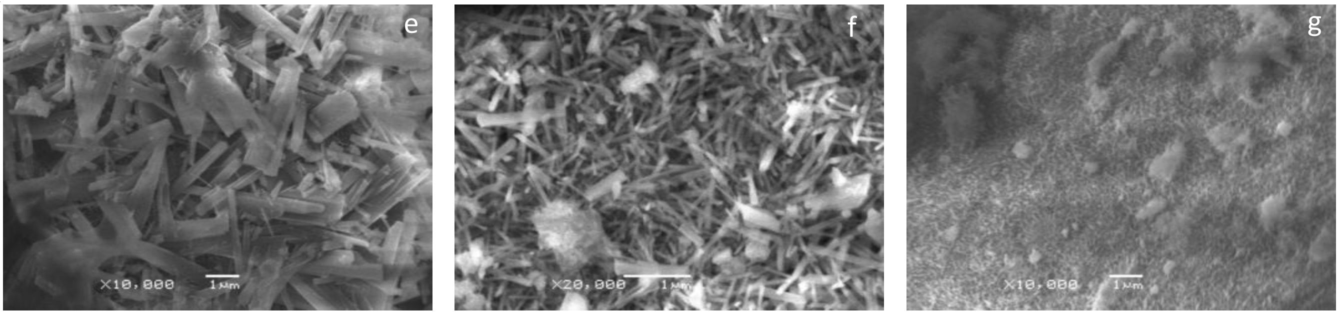

Fig. 4. SEM images of product with calcining temperature (e = 850 °C, f = 900 °C, g = 950 °C)

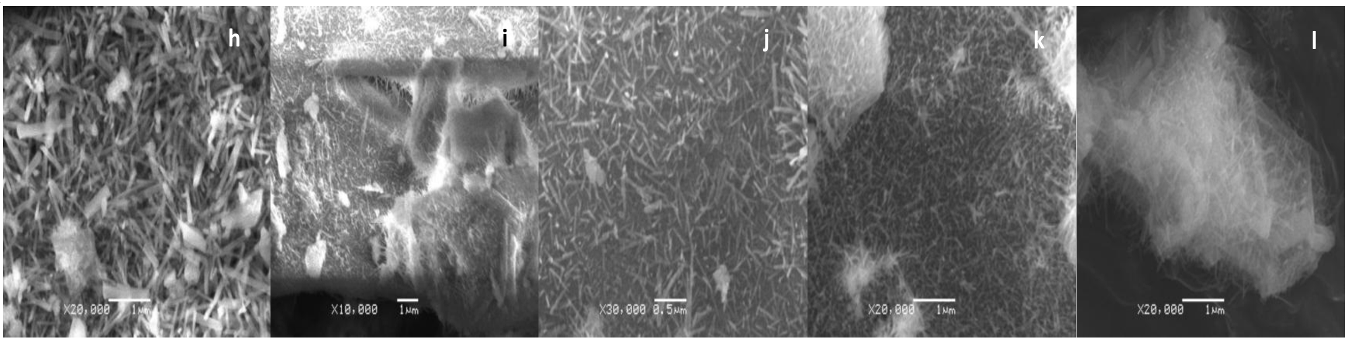

Fig. 6 SEM of aluminum borate nanowires with the change of dispersing agent (e) citric acid, (f) tartaric acid, (g) L-tartaric acid, (h) D-tartaric acid and (i) lactic acid)

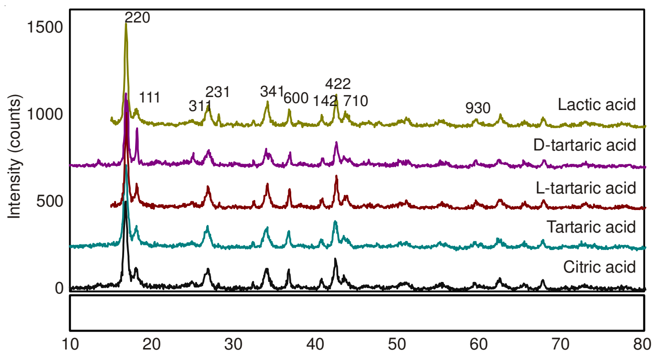

Fig. 7 XRD pattern of the product with calcining temperature (K = 900 °C) with the different of dispersing agent (h) citric acid, (i) tartaric acid, (j) L-tartaric acid, (k) D-tartaric acid and (l) lactic acid

experiment, accordingly. In Fig. 7, it is clearly seen that the abundant fiber-like structures. These fibers often grow closely together, the level diameter was in the range of about 50-90 nm, the lengths of these fibers are around 10-30 μm.

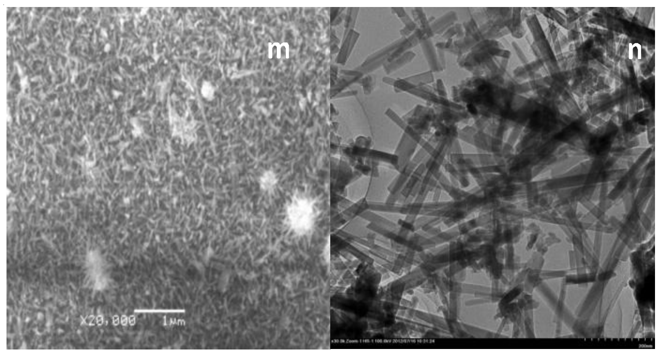

Fig. 8. SEM and TEM images of the product in large scale production

The XRD pattern (Fig. 9) of the ten times scale-up experiment product identified the formation of an aluminum borate ($Al_4B_2O_9$) nanowires at 900 °C for 2 h while the L-tartaric acid were used as dispersing agent, $Al_4B_2O_9$, the fitting crystalling parameters are a = 14.74 Å, b = 15.26 Å and c = 5.557 Å (JCPDS-ISD, PDF#29-0010) was the only phase. It was seen that inductive effect was good as L-tartaric acid was used as dispersing agent.

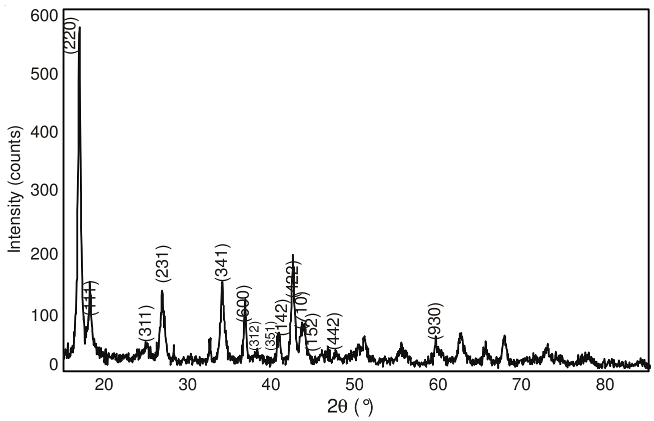

Fig. 9. XRD pattern of the scale-up production

In summary, aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) powders were used as starting materials. L-Tartaric acid was added to serve as dispersing agent. A sol-gel process followed by annealing was employed to fabricate single crystal aluminum borate ($Al_4B_2O_9$) nanowires. Ten times scale-up experiment product with a diameter in the range of about 50-90 nm and the lengths around 10-30 μm. It was to be promising in a large-scale production of aluminum borate ($Al_4B_2O_9$) nanowires.

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