Journal of Solid State Chemistry 197 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Growth process of $Cu_2Al_6B_4O_{17}$ whiskers

Chengcai Zhu [a,b], Xueying Nai [a], Donghai Zhu [a,b], Fengqin Guo [c], Yongxing Zhang [a,b], Wu Li [a,*]

[a] Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] Department of Basin Education, Qinghai University, Xining 810016, PR China

ARTICLE INFO

Article history:
Received 19 May 2012
Received in revised form
2 August 2012
Accepted 5 August 2012
Available online 23 August 2012

Keywords:
Crystal growth
Whisker
Copper aluminum borate

ABSTRACT

The reactions occurred and growth process in the preparation of copper aluminum borate ($Cu_2Al_6B_4O_{17}$) whiskers based on flux method ($Al_2(SO_4)_3/CuSO_4/H_3BO_3$ as raw materials, K_2SO_4 as flux) were investigated. The thermogravimetric and differential scanning calorimetry analysis (TG-DSC), inductively coupled plasma atomic emission spectrum analysis (ICP-AES) and X-ray diffraction analysis (XRD) results of reactants mixture quenched at various temperatures and phase diagrams of K_2SO_4–$Al_2(SO_4)_3$ system and B_2O_3–Al_2O_3 system showed that the reaction process proceeds through three steps: the formation and decomposition of two different kinds of potassium aluminum sulfate ($K_3Al(SO_4)_3$ and $KAl(SO_4)_2$); the formation of aluminum borate ($Al_4B_2O_9$) and decomposition of copper sulfate ($CuSO_4$) and boric acid (H_3BO_3); growth and formation of copper aluminum borate ($Cu_2Al_6B_4O_{17}$) whiskers. The scanning electron microscopy (SEM) analysis results indicated that morphology in growth of $Cu_2Al_6B_4O_{17}$ whiskers develops through three stages: nanoparticles, fan-shaped whiskers and agminate-needlelike whiskers.

1. Introduction

One-dimensional nanoscale materials, such as nanotubes, nanowires, and nanobelts, have attracted much attention both because of their high tensile property [1,2] and other potential applications. In recent years, inorganic fibers and whiskers have been used mostly as reinforcements in composites and thermal insulation. Various fibrous materials such as glass, carbon, SiC, aluminum borate ($Al_{18}B_4O_{33}$), Al_2O_3, etc., are prepared for such purpose [3]. However, the preparation and application of carbon, SiC and Al_2O_3 whiskers are limited because of the difficult processing method and high cost. The studies of preparations and applications of metal borate whiskers, such as aluminum borate [4–6] and magnesium borate [7–11], are popular research fields in recent years owing to their excellent MOE (modulus of elasticity), intensity and other properties. Most of the metal borate whiskers used as reinforcement in alloy, ceramics are produced by high-temperature sintering [4,12,13]. However, few of researches are focused on reaction and growth process of the whiskers [14].

Copper aluminum borate ($Cu_2Al_6B_4O_{17}$) whisker is a kind of novel double salt borate whisker. The preparation of $Cu_2Al_6B_4O_{17}$ whisker has been reported by us recently [15], but factors affect the preparation of $Cu_2Al_6B_4O_{17}$ whisker, such as heating temperature, heating time, flux type, reactants ratio, reaction process, growth process and so on, need be studied comprehensively in order to prepare $Cu_2Al_6B_4O_{17}$ whiskers effectively and control morphology of $Cu_2Al_6B_4O_{17}$ whiskers. In this contribution, the reaction process and growth process of $Cu_2Al_6B_4O_{17}$ whiskers were researched by X-ray diffraction (XRD), thermogravimetry (TG), plasma spectrometer, SEM and phase diagrams of the $Al_2(SO_4)_3$–K_2SO_4 system and B_2O_3–Al_2O_3 system.

2. Experimental

2.1. Synthesis

All the chemical reagents used in this experiment were of analytical grade and pulverized in grinder. Copper sulfate ($CuSO_4$), boric acid (H_3BO_3), aluminum sulfate octadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$), and potassium sulfate (flux, K_2SO_4) powders were used as reagents. These reagents were accurately weighed in a proper amount (Cu:Al:B=2:6:8; total weight 13 g) and the K_2SO_4 addition was 40 wt%. The mixture was further grinded and sieved by 120 mesh screen.

The mixtures were placed in a corundum crucible (50 ml), heated (10 °C/min) to 870 °C and kept for 240 min at 870 °C, then cooled down to room temperature (1 °C/min). During the whole reaction process, samples in different stages were taken out from furnace and quenched with liquid nitrogen (Table 1). As Table 1 shows, samples 1–5 are from heating process, samples 6–8 are

* Corresponding author.
E-mail addresses: zccgn2012@163.com, liwu@isl.ac.cn (W. Li).

0022-4596/$ - see front matter Crown Copyright © 2012 Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.08.013

Table 1
Sampling in different reaction stages.

Number	Sampling stage	Temperature (°C)	Thermostatic time (min)
1	Heating	600	0
2		700	0
3		800	0
4		840	0
5		870	0
6	Constant Temperature	870	30
7		870	120
8		870	240
9	Cooling	700	0
10		600	0
11		500	0

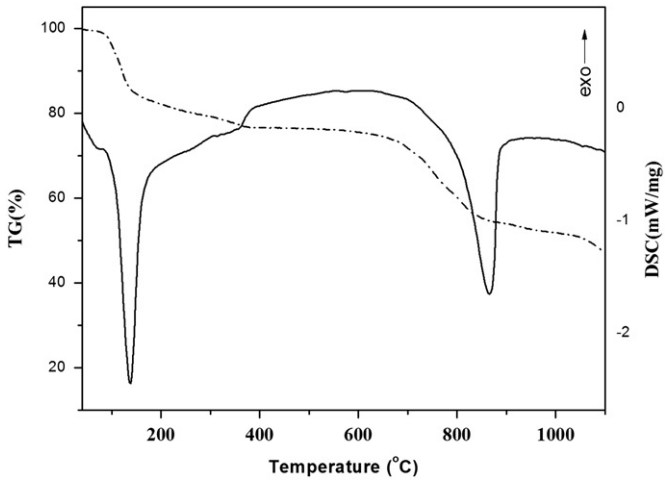

Fig. 1. TG-DSC curve of mixture of the raw materials.

from constant temperature process, samples 9–11 are from cooling process.

2.2. Characterization

The quenched products were identified by X-ray diffraction (XRD, PANalytical X'Pert PRO diffractometer with Cu$K\alpha$ radiation, λ=0.15406 nm), thermogravimetric and differential scanning calorimetry (STA449F3 analyzer) and inductively coupled plasma atomic emission spectrometer (ICAP 6500 DUO). The morphology of the whiskers was characterized by scanning electron microscopy (SEM, JSM-5610LV, JEOL).

3. Results and discussion

3.1. Reaction process

Fig. 1 shows the TG-DSC curve of the mixture of raw materials (Cu:Al:B=2:6:8) and the K_2SO_4 addition was 40 wt%, which was heated from the room temperature to 1100 °C. It is obvious that two different endothermic peaks (138 °C and 866 °C) can be seen in the DSC curve, corresponding to the two different weight loss processes in the TG curve, respectively. In the first stage, H_3BO_3 decomposes and $Al_2(SO_4)_3 \cdot 18H_2O$ dehydrates when the temperature range is 100–400 °C. The weight loss in the temperature range of 100–400 °C is 24.53%, closely corresponding to the theoretical content of water of 25.42%. Few crystal water of $CuSO_4$ dehydrates about 240–320 °C. In the second stage, K_2SO_4 melts as flux at about 750 °C. $CuSO_4$ and $Al_2(SO_4)_3$ break down to activated CuO and Al_2O_3 when the temperature range is 700–950 °C. Two steps exist when $CuSO_4$ is decomposing to CuO and SO_3. First, $CuSO_4$ decomposes to $CuSO_4 \cdot CuO$ and SO_3 from 670 to 820 °C. Then $CuSO_4 \cdot CuO$ decomposes to CuO and SO_3 from 850 to 900 °C [16]. The weight loss in the temperature range of 700–950 °C is 18.71%, closely corresponding to the theoretical content of sulfur trioxide (18.82%). Weight loss of the mixture of the reactants indicates that the temperature ranging from 700 to 950 °C is proper to form $Cu_2Al_6B_4O_{17}$ whisker. However, the TG-DSC results just indicated the weight loss and ex-endothermal process of the mixture, but cannot give the exact composition of intermediate products.

X-ray diffraction (XRD) patterns of quenched samples at different temperatures are described in Fig. 2. All samples were treated by hot water to remove impurities (K_2SO_4). The XRD result in Fig. 2 shows that compound compositions of the intermediate samples are changing along with the calcination temperature and time. Samples 1 and 2 were dissolved absolutely in water. There are four compounds identified by XRD: monopotassium aluminum sulfate ($KAl(SO_4)_2$), tripotassium aluminum sulfate ($K_3Al(SO_4)_3$), aluminum borate ($Al_4B_2O_9$) and copper aluminum borate ($Cu_2Al_6B_4O_{17}$). Only $KAl(SO_4)_2$ and $K_3Al(SO_4)_3$ were observed before 870 °C (samples 3 and 4). At 870 °C, the diffraction peaks of $K_3Al(SO_4)_3$ disappeared and that of the $KAl(SO_4)_2$ existed (sample 5). The intermediate product ($Al_4B_2O_9$) and final product ($Cu_2Al_6B_4O_{17}$) formed gradually at constant temperature process at 870 °C (samples 6–8). Fig. 2 (samples 6–8) shows characteristic peaks of products (2θ): 16.7, 26.6, 33.8 and 43.5. The same characteristic peaks for $Al_4B_2O_9$ and $Cu_2Al_6B_4O_{17}$ mean that the existence of crystal phase transitions from $Al_4B_2O_9$ to $Cu_2Al_6B_4O_{17}$. The result of XRD indicates that $Cu_2Al_6B_4O_{17}$ is derived from $Al_4B_2O_9$. Boric acid and copper sulfate were not detected in the samples even before heating, owing to its relatively low concentration and amorphous forms.

XRD results just identify crystal compound, but some intermediate products, such as CuO, B_2O_3, are still in amorphous forms when quenching from high to room temperature. Fig. 3 shows color change of intermediate products which were treated by hot distilled water to remove water-soluble compounds. In heating

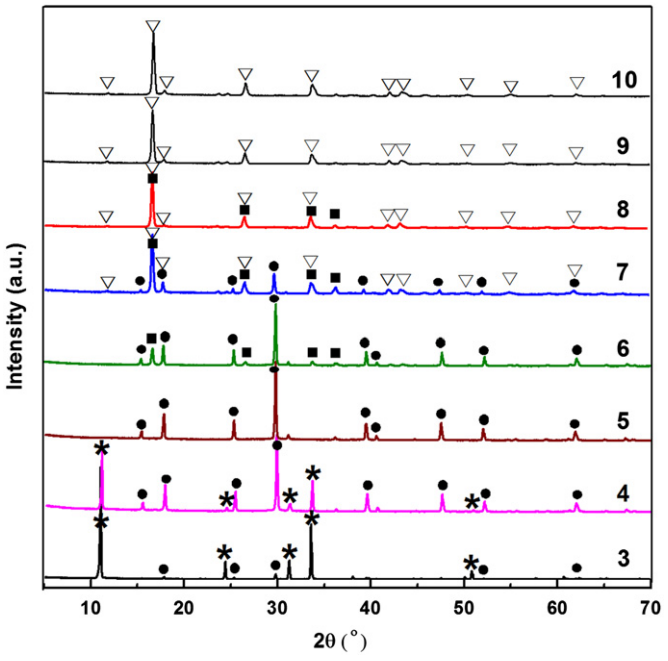

Fig. 2. Composition changes of intermediate product. Sample sequence is corresponding to Table 1. ★—$K_3Al(SO_4)_3$, ●—$KAl(SO_4)_2$, ■—$Al_4B_2O_9$, ▽—$Cu_2Al_6B_4O_{17}$.