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Novel hydrothermal synthesis of tobermorite fibers using Ca(II)-EDTA complex precursor

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Abstract

A novel method for synthesizing large size tobermorite fibers without special instruments, high temperature and long time was developed. Tobermorite fibers with 40–100 μm in length and 0.1–1 μm in diameter were hydrothermally synthesized at 200 °C for 5 h using a Ca (II)-EDTA complex precursor. And the effect of experiment conditions on the phase, morphology and composition of final products were investigated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ca(II)-EDTA complex precursor; Fibers; Hydrothermal synthesis; Tobermorite fibers

1. Introduction

Preparation of calcium silicate hydrate fibers, especially xonotlite and tobermorite, has been attracting attention in recent years. This arises from the fact that these fibers are widely required in modern industry because of their high stability at high temperature and fibrous crystal form.[1,2] They are usually prepared from suspension of silica and calcium hydroxide by hydrothermal treatment.[3–5] However, long fibers are generally difficult to obtain and the experiment results were affected by series factors, such as composition, crystallization, size distribution of raw materials and the weight ratio of water/solid material.[3–5] Although several reports concerning hydrothermal synthesis of long calcium silicate hydrate fibers were reported in the literature, high temperature (250–350 °C), long time (72–200 h) and special instrument (continuous-type or multichamber autoclave) were needed in their experiments.[6,7]

To break these limitations, we proposed a use of Ca^{2+} chelated complex as Ca^{2+} source in hydrothermal synthesis of calcium silicate hydrate fibers. And the object of this work is to investigate the effect of starting conditions, such as the starting Ca/Si molar ratio, treatment time and pH value, on the phase, morphology and composition of final products.

2. Experimental procedures

Starting materials were special reagent grade $Ca(OH)_2$, Aerosol (amorphous SiO_2) and ethylenediaminetetraacetic acid (EDTA). Calcium-EDTA was prepared by mixing $Ca(OH)_2$ and EDTA in appropriate quantities in deioned water, together with the desired amount of KOH to adjust the solution pH. Then Aerosol (amorphous SiO_2) was added and the pH was adjusted again till the solution became clear. The molar ratio of EDTA/Ca^{2+} was 1.0 and the concentration of silicon ion Si^{4+} was 0.02M in all cases. The experiment starting conditions were shown in Table 1 in detail. Each solution was poured into an autoclave, and hydrothermally treated at 200 °C under the pressure of 2 MPa for various times. After the treatments, the precipitated solid phases were filtrated, washed several times with deioned water and dried at 80 °C for 24 h.

The phase composition of the samples was characterized by X-ray diffraction (XRD) (Model D/max 2550V,

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Table 1
Starting conditions and final Ca/Si results in the present work

	Group 1				Group 2				Group 3
	1-1	1-2	1-3	1-4	2-1	2-2	2-3	2-4	3-1
Starting Ca/Si	1.0	1.25	1.5	2.0	2.0	2.0	2.0	2.0	2.0
Treatment time (h)	5	5	5	5	1	3	5	10	10
Starting pH	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	12.0
Final Ca/Si	0.71	0.72	0.73	0.74	0.67	0.68	0.71	0.74	0.64

Rigaku Co., Japan) with CuK_α radiation (40 KV and 40 mA). Scanning electron microscope (SEM) (Model EPMA-8705QH$_2$, Shimadzu Co., Japan) was used to observe their morphologies. Chemical composition was analyzed by Energy Dispersive Spectrometer (EDS) (Model TN-5502N, Noran Co, America).

3. Results and discussion

The effect of varying Ca/Si molar ratio from 1.0 to 2.0 was investigated with pH = 13.0 and treatment time of 5 h. The final products were all tobermorite with almost identical XRD pattern and morphology. As shown in Fig. 1(A) the final products had good crystallinity. High intensity of (*00l*), (*h0l*) diffraction and low intensity of (*0k0*) in the XRD patterns suggested that the obtained tobermorite fibers grow in the *b*-axis direction. Fig. 2(a). shows that the final products were needle-like fibers and not agglomerated, with 40–100 μm in length and 0.1–1 μm in diameter. While at the same time, the Ca/Si molar ratios of the final product increased with the increase of starting Ca/Si molar ratio (Table 1, Group 1). These results indicated that starting Ca/Si molar ratio didn't make so great a difference to the phase and morphology as it did to the chemical composition on the final products.

The effect of varying treatment time from 1 to 10 h was investigated with pH = 13.0 and starting Ca/Si molar ratio of 2.0. The products treated for 1 h could not be identified by X-ray diffraction because of their limited amount. As shown in Fig. 1(B)–(D), pure tobermorite of good crystallinity was obtained after 3 h treatment. And the diffraction intensity of (002), (101), (110) and (112) peaks increased with increasing of treatment time, which indicated that the tobermorite fibers grew longer and had sharper ends. This was confirmed in Fig. 2(b)–(d) The crystals split and grew, changing from short and platy form to long and needle-like fibers. After 5 h treatment, the fibers had length and width in the ranges of 40–100 and 0.1–1 μm, respectively. Additionally, the Ca/Si molar ratio of final products correlated positively with the starting Ca/Si molar ratio (Table 1, Group 2).

The effect of pH on the chemical composition and morphology was investigated with starting Ca/Si molar ratio of 2.0 and treatment time of 10 h. When the pH value of starting solution was 12.0, the obtained tobermorite had a lower Ca/Si molar ratio of 0.64 (Table 1, Group 3) and took on the platy form dramatically (Fig. 3). It was reported that platy tobermorite split and transformed to needle-like fibers after soaking in the 2M KOH solution at 180 °C for 5 days.[8] These results were mainly attributed to the different arrangements of Si–O tetrahedrons during the tobermorite crystals' growth. In this study, chain structures were formed by Si–O tetrahedrons at pH 13.0 while layer structures were formed at pH 12.0, which resulted in differences in the morphologies of final products.

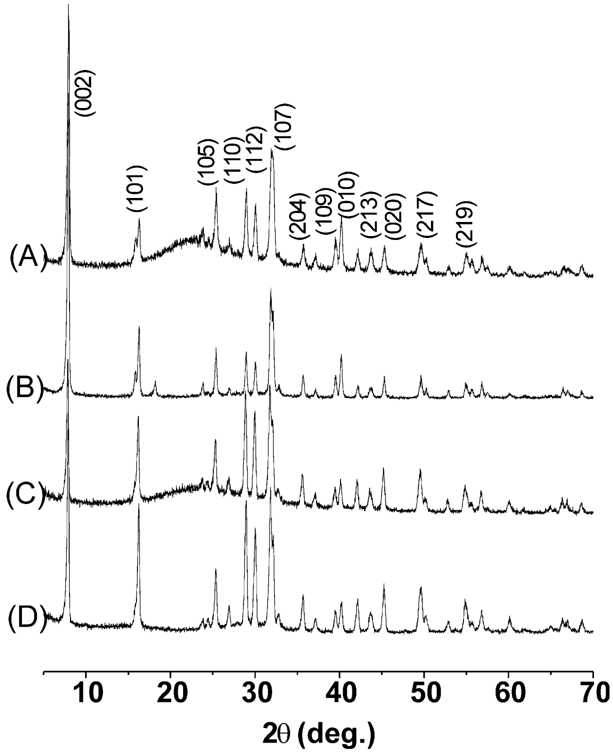
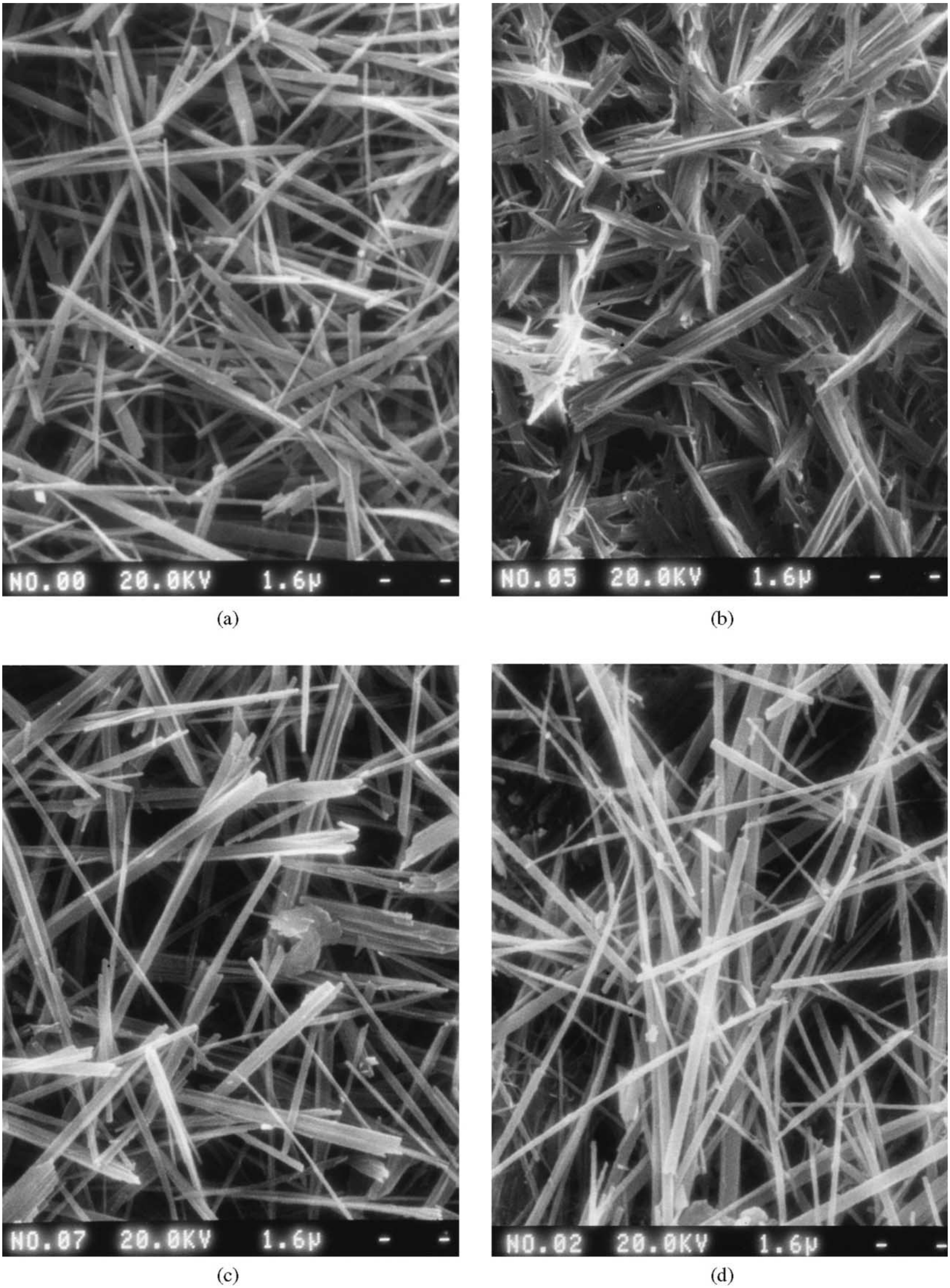


Fig. 1. XRD patterns of tobermorite prepared from Groups 1 and 2: (A) Ca/Si = 1.0, 5 h; (B) Ca/Si = 2.0, 3 h; (C) Ca/Si = 2.0, 5 h; (D) Ca/Si = 2.0, 10 h.



(a) (b) (c) (d)

Fig. 2. SEM photographs of tobermorite fibers prepared at pH = 13 and various starting Ca/Si ratios, reaction times: (A): Ca/Si = 1.0, 5 h; (B)–(D) Ca/Si = 2.0, 1, 3, 5 h.

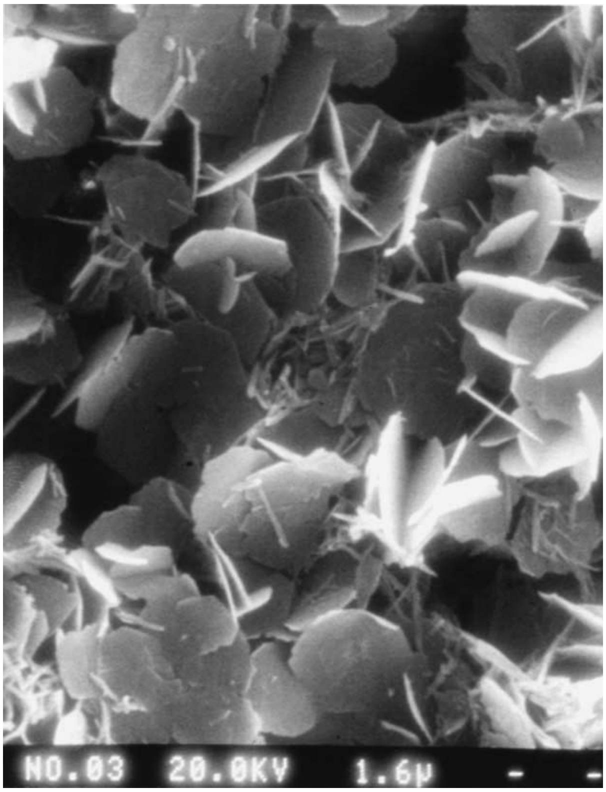


Fig. 3. SEM photographs of plate-like tobermorite prepared at pH = 12, Ca/Si = 2.0, 10 h.

4. Conclusions

Tobermorite fibers have been hydrothermally prepared at 200 °C from the solution containing calcium and silicon ions and EDTA as a chelating agent. After 5 h treatment, the width, length and aspect ratio of the fibers are in the ranges of 0.1–1 μm, 40–100 μm and 20–80, respectively.

Experiment conditions had important effect on the final products. The starting Ca/Si molar ratio did not make great difference to the phase and morphology of tobermorite but it determined the final composition. Tobermorite fibers split, became longer and got higher Ca/Si molar ratio as the treatment time increased. When the starting pH value was 12.0, tobermorite of plate-like form and low Ca/Si molar ratio was produced.

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