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Hydrothermal synthesis of xonotlite from carbide slag

Jianxin Cao *, Fei Liu, Qian Lin, Yu Zhang

Department of Chemical Engineering, Guizhou University, Guiyang 550003, China

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Abstract

Carbide slag was used as the calcareous materials for the first time to prepare xonotlite via dynamic hydrothermal synthesis. The effects of influential factors including different calcination temperatures, pretreatment methods of the carbide slag and process parameters of hydrothermal synthesis on the microstructure and morphology of xonotlite were explored using XRD and SEM techniques. The results indicate that the carbide slag after proper calcination could be used to prepare pure xonotlite; and different calcination temperatures have little effect on the crystallinity of synthesized xonotlite, but have great impact on the morphology of secondary particles. The different pretreatment methods of the carbide slag pose great impact on the crystallinity and morphology of secondary particles of xonotlite. Xonotlite was also synthesized from pure CaO under the same experimental conditions as that prepared from calcined carbide slag for comparison. Little amount of impurities in carbide slag has no effect on the mechanism of hydrothermal synthesizing xonotlite from carbide slag.

Keywords: Hydrothermal synthesis; Carbide slag; Xonotlite; Calcination temperature

1. Introduction

Carbide slag is an industrial waste produced by calcium carbide hydrolysis to prepare C_2H_2 gas, PVC, etc. Millions of tons of carbide slag were accumulating in many chemical industries every year, polluting the environment [1,2]. Nowadays, people are becoming more aware of solid waste pollution and are seeking solutions to a cleaner planet. Accordingly, recycling carbide slag has aroused wide interests in many researchers.

Xonotlite (calcium silicate) is an ultra-light insulation material. It has been widely used in industry for its low thermal conductivity, wide applying temperature range, environment friendliness and low density [3–5]. In a general way, the crystal of xonotlite stays in nemaline or needle shape, and these could, under certain conditions of hydrothermal synthesis, form orbicular particles via the method of churning up. Synthesizing a significant amount of the orbicular particles is of utmost importance in preparing ultra-light thermal insulation material of xonotlite-calcium silicate, and xonotlite is synthesized via hydrothermal processing, by using kiesel and calcareous materials as the raw materials (with $CaO/SiO_2 \approx 1:1$) [6,7]. So far, much work has been done on the synthesis of xonotlite using quicklime as the calcareous material. As a result, the ecosystem was destroyed badly by mining a large quantity of limestone which was used to produce quicklime.

Carbide slag consists primarily of CaO and also contains some impurities such as Al_2O_3, SiO_2, Fe_2O_3, MgO, and SO_3. So, carbide slag can be recycled to produce ultra-light thermal insulation material of xonotlite-calcium silicate, reducing the environmental pollution of industrial waste.

In the study of the carbide slag as a raw material for the preparation of xonotlite, the effects of influential factors including different calcination temperatures, pretreatment methods of carbide slag and process parameters of

* Corresponding author. Tel.: +86 13985198689; fax: +86 851 8115839.
E-mail address: jxcao@gzu.edu.cn (J. Cao).

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hydrothermal synthesis on the microstructure and morphology of synthesized xonotlite were studied in this investigation. Then, the production cost of xonotlite would be reduced tremendously on account of the low cost carbide slag which is an industrial waste. On the other hand, this method recycles carbide slag instead of using quicklime as raw material, and thus is environmentally benign.

2. Experimental

2.1. Materials

Carbide slag and pure CaO were used to prepare xonotlite as calcareous materials, and theirs contents are given in Table 1. Silica fume with $SiO_2 > 98\%$ was used to prepare xonotlite as the kiesel materials.

2.2. Preparation of xonotlite slime

The original of carbide slag and pure CaO was of a median particle less than 75 μm. And carbide slag was calcined at different temperatures (e.g., 700, 800, 900, and 1000 °C) for 2 h in a ceramic crucible with a thickness of 40 mm.

The starting materials were mixtures of CaO (prepared by calcination of carbide slag at different temperatures for 2 h) and silica fume (with a median particle diameter less than 75 μm). These starting materials were autoclaved with stirring in a 1 L reaction chamber. The hydrothermal treatment proceeded under the following conditions: CaO/SiO_2 mol ratio of 1.0, water/solid weight ratio of 30, at a certain time from 0 to 10 h and a certain temperature from 205 to 225 °C.

2.3. XRD and SEM of xonotlite slime

Xonotlite slime dried in a vacuum desiccator at 105 °C was studied by scanning electron microscope (SEM). The powder of xonotlite with a median particle diameter less than 75 μm was examined by X-ray diffraction (XRD).

3. Results and discussion

3.1. Effect of different calcination temperatures on morphology and crystallinity of synthesized xonotlite

X-ray diffraction patterns of the xonotlite slime prepared from the carbide slag calcined at 700 and 1000 °C are shown in Fig. 1. The results indicate that the hydrothermally derived calcium silicate phases were confirmed to be highly crystalline xonotlite phases.

Table 1
Chemical contents of carbide slag and pure CaO (wt.%)

Materials	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	Others
Carbide slag	66.190	2.00	0.450	2.560	0.120	1.200	6.200
CaO	98.000	–	0.015	–	0.500	0.100	1.390

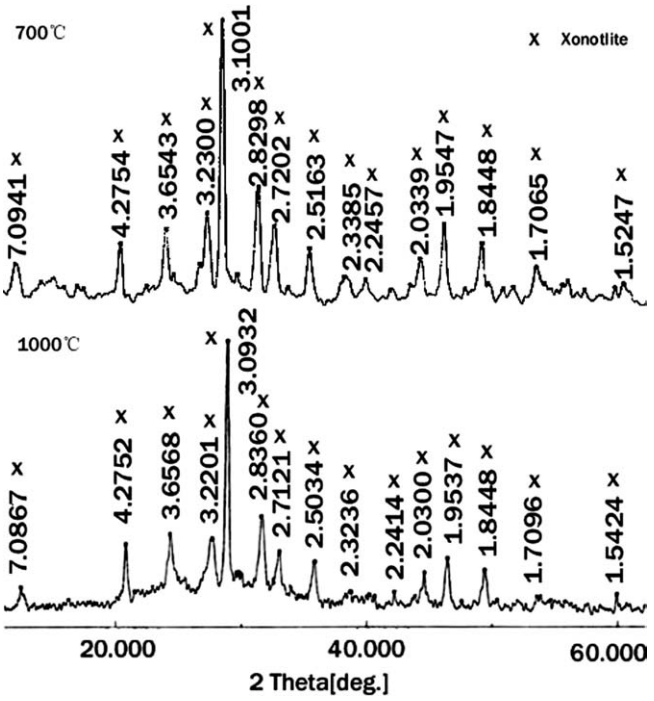

Fig. 1. XRD patterns of xonotlite synthesized by calcined sample at 700 and 1000 °C.

SEM images of the xonotlite slime prepared from the carbide slag calcined at 700, 800, 900, and 1000 °C are presented in Fig. 2. The images indicate that the orbicular secondary particles of xonotlite prepared from carbide slag calcined at 700 and 800 °C are in the range of 10–20 μm in diameter, while the xonotlite prepared from carbide slag calcined at 900 and 1000 °C are smaller and these orbicular secondary particles stay in clusters.

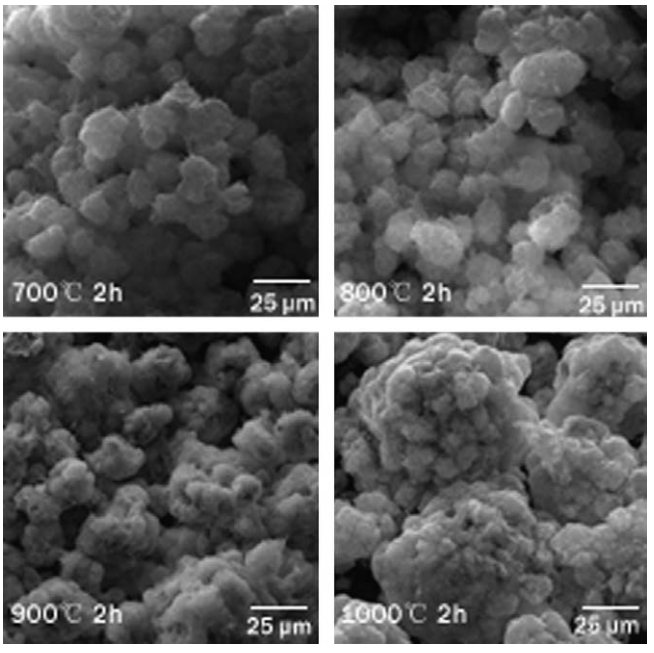

Fig. 2. SEM images of xonotlite synthesized by four-calcined carbide slag.

The XRD and SEM results show that different calcination temperatures of the carbide slag have little effect on the crystallinity of synthesized xonotlite, but pose significant impact on the morphology of secondary particles.

3.2. Effect of different pretreatment methods of carbide slag on morphology and crystallinity of synthesized xonotlite

The X-ray diffraction patterns and SEM images of xonotlite synthesized from pure CaO, calcined and original carbide are shown in Figs. 3 and 4. It can be seen from Fig. 3a ($d = 0.69974$; 0.42509; 0.36333; 0.32292; 0.30806; 0.28151; and 0.26994) that xonotlite is the only crystalline phase, and from Fig. 3b and c that xonotlite is also the main crystalline phase. However, the hydrothermally prepared calcium silicate phase shown in Fig. 3b ($d = 0.70867$; 0.42752; 0.36568; 0.32201; 0.30932; 0.28360 and 0.27376) was confirmed to be a higher xonotlite phase than that shown in Fig. 3c ($d = 0.71206$; 0.42348; 0.36927; 0.30536; 0.28204 and 0.27376).

The SEM images (Fig. 4a and b) show that the xonotlite crystals synthesized by calcined carbide slag mainly consist of tiny needle-like micro-fibers together with orbicular particles. But it can be seen that the xonotlite fibers are shorter in length (Fig. 4c). SEM images of the samples also indicate that the structure of xonotlite synthesized from the calcined carbide slag was the same as that prepared from pure CaO.

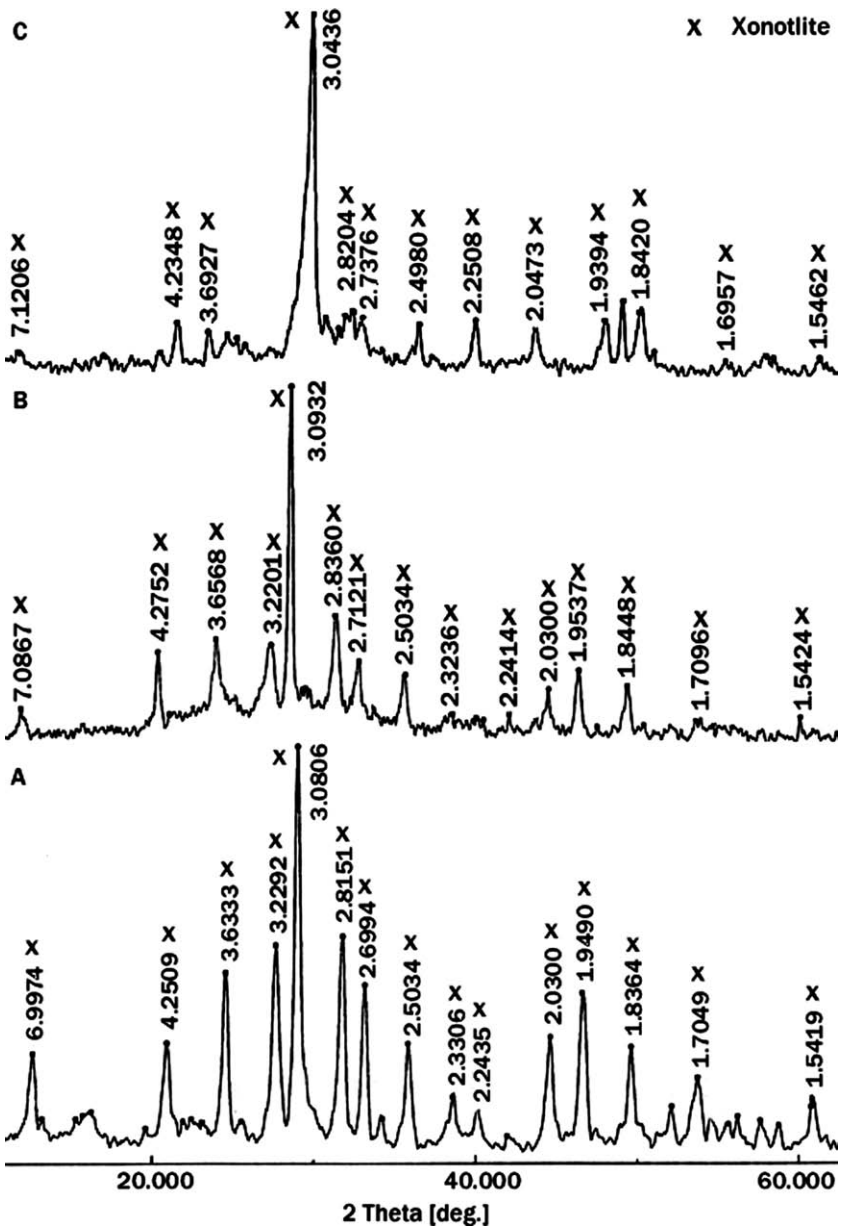

Fig. 3. XRD patterns of synthesized xonotlite. (A) Xonotlite synthesized from pure CaO; (B) xonotlite synthesized from calcined carbide slag; (C) xonotlite synthesized from original carbide slag.

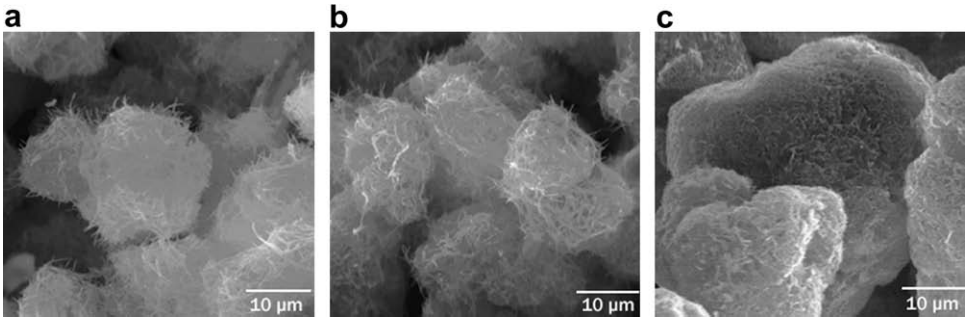

Fig. 4. SEM images of xonotlite synthesized from pure CaO and carbide slag pretreated with different methods. (a) Xonotlite synthesized from pure CaO; (b) xonotlite synthesized from calcined carbide slag; (c) xonotlite synthesized from original of carbide slag.

Both xonotlites are comprised of large orbicular particles of similar size.

The XRD and SEM results illustrate that different pretreatment methods of carbide slag posed significant impact on the crystallinity and morphology of secondary particles of xonotlite. As shown in Table 1, carbide slag contains more impurities than CaO.

However, the results show that such little amount of impurities in carbide slag have no effect on the microstructure and morphology of synthesized product.

3.3. Effect of process parameters of hydrothermal synthesis on morphology and crystallinity of synthesized xonotlite

3.3.1. Effect of reaction temperature and pressure on synthesized xonotlite

The X-ray diffraction patterns of xonotlite prepared at different temperatures and pressures are shown in Fig. 5. At 205 °C/1.9 MPa, a large amount of xonotlite together with small quantities of tobermorite was found. Tobermorite together with xonotlite was produced in the samples under this hydrothermal condition. At 215 °C/2.1 MPa and 225 °C/2.4 MPa, there was only xonotlite phase in the samples. Therefore, at high temperatures and pressures, pure xonotlite can be obtained.

3.3.2. Effect of reaction time on synthesized xonotlite

The change of the crystalline structure with different reaction times can be observed in Fig. 6. Both the xonotlite and the tobermorite phases in the samples prepared for 6 h were found. When the reaction time is over 8 h, xonotlite is the only crystalline phase in the samples.

The discussions made above present clear information that pure xonotlite was prepared successfully by using the calcined carbide slag under the conditions of $CaO/SiO_2 = 1.0$, a water/solid ratio of 30/1, 215 °C/2.1 MPa and reaction time for 8 h. Since the experimental conditions of xonotlite synthesized from calcined carbide slag were almost the same as that from pure CaO [8], it can be concluded that little amount of impurities in carbide slag has no effect on the product at controlled experimental conditions.

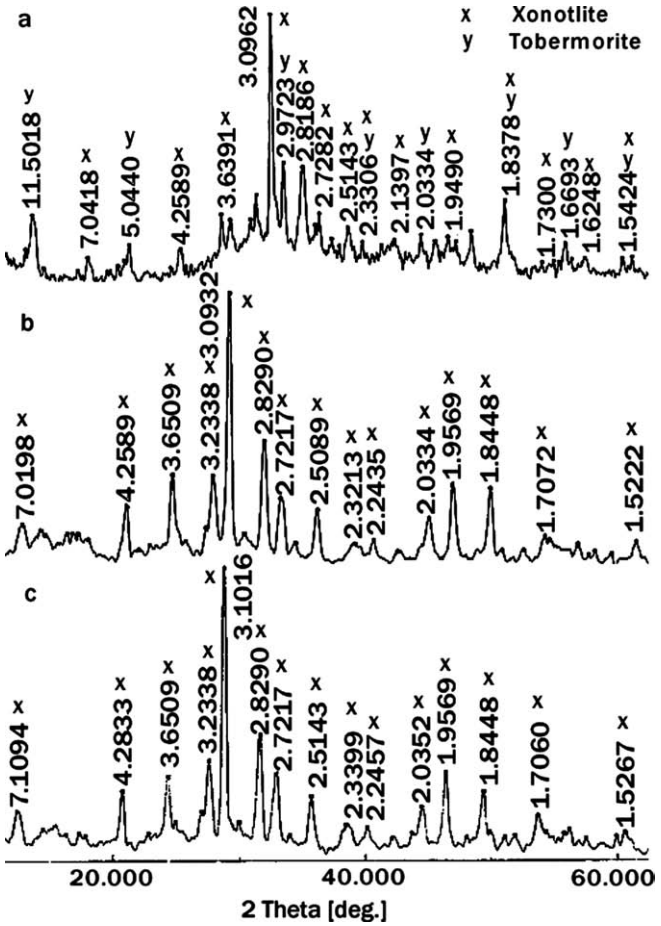

Fig. 5. XRD patterns of xonotlite synthesized at different temperatures and pressures. (a) 205 °C/1.9 MPa 8 h; (b) 215 °C/2.1 MPa 8 h; (c) 225 °C/2.4 MPa 8 h.

3.4. The mechanism of hydrothermal synthesizing xonotlite from carbide slag

The samples, synthesized for 0, 0.5, 1, 3, 5 and 8 h under the conditions of $CaO/SiO_2 = 1.0$, a water/solid ratio of 30/1, 215 °C/2.1 MPa, were studied by XRD and SEM, as shown in Figs. 7–12.

From the SEM image shown in Fig. 7, the flocculent C–S–H (II) (calcium silicate hydrates) was firstly prepared for 0 h after increasing the temperature of hydrothermal

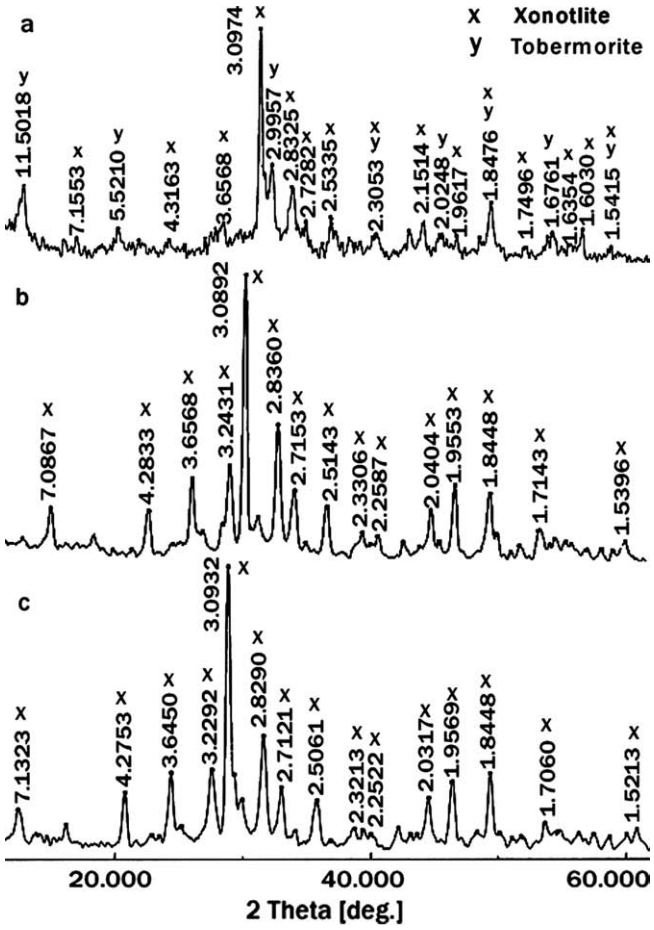

Fig. 6. XRD patterns of xonotlite synthesized with different reaction time. (a) 220 °C 6 h; (b) 220 °C 8 h; (c) 220 °C 10 h.

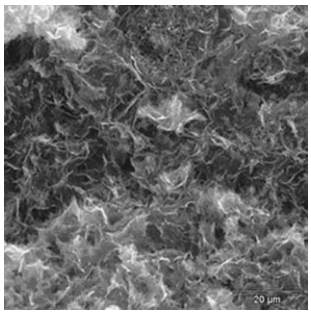

Fig. 7. SEM image of product synthesized for 0 h.

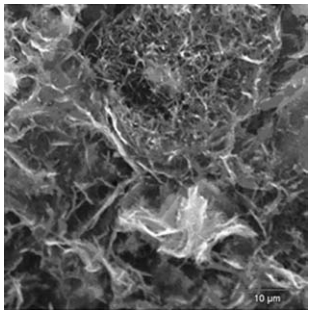

Fig. 8. SEM image of product synthesized for 0.5 h.

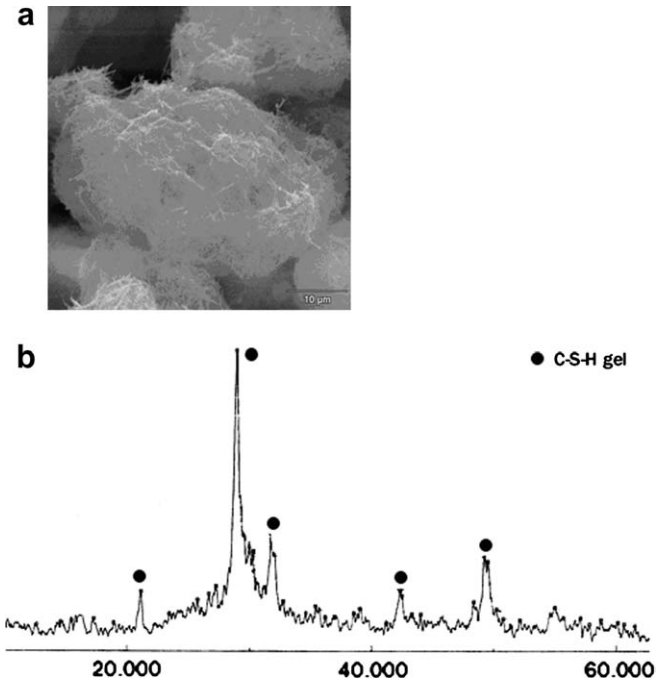

Fig. 9. SEM image (a) and XRD pattern (b) of product synthesized for 1 h.

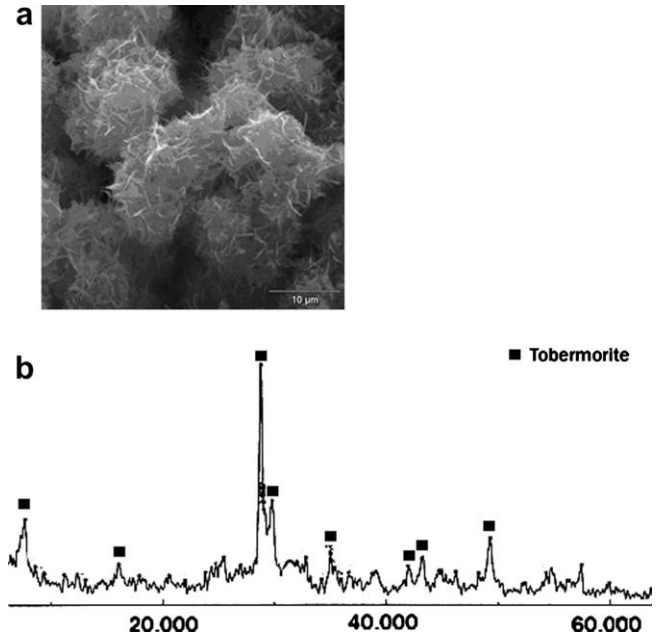

Fig. 10. SEM image (a) and XRD pattern (b) of product synthesized for 3 h.

synthesis from room temperature to 215 °C. Both the flocculent C–S–H (II) and the fibriform C–S–H (I) which was transformed from C–S–H (II) were found in the sample prepared for 0.5 h (Fig. 8). As shown in Fig. 9, the C–S–H (II) disappeared and there was only C–S–H (I) in the sample of 1.5 h. From Fig. 10b, the XRD results show that C–S–H (I) disappeared, and petaline tobermorite particles were found in the sample of 3 h as shown in Fig. 10a.

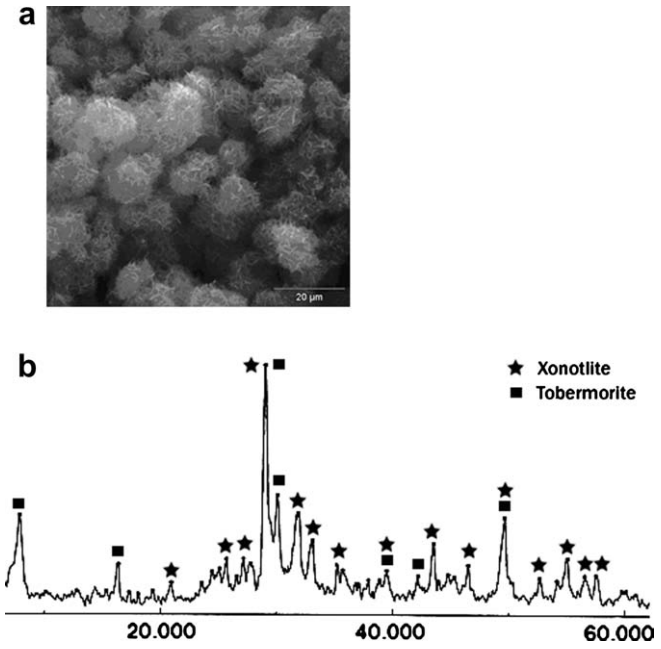

Fig. 11. SEM image (a) and XRD pattern (b) of product synthesized for 5 h.

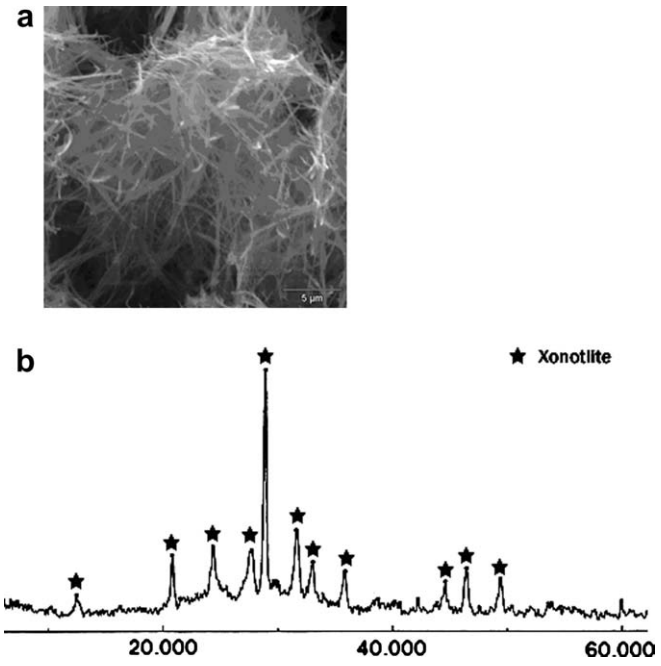

Fig. 12. SEM image (a) and XRD pattern (b) of product synthesized for 8 h.

The presence of both tobermorite and xonotlite is confirmed for the sample with a treatment time of 5 h, as shown in Fig. 11, indicating the transformation of crystals from tobermorite to xonotlite. And lastly, there was only spiculate xonotlite crystal in the sample of 8 h (Fig. 12).

From the above discussion, we could conclude that the mechanism of hydrothermal synthesis of xonotlite from carbide slag is as follows:

$$C-S-H(\text{¢ó}) \rightarrow C-S-H(\text{¢ñ}) \rightarrow \text{tobermorite} \rightarrow \text{xonotlite}$$

It is not difficult to find that the mechanism is the same as that for pure CaO [9]. In this case, it can be concluded that little amount of impurities in carbide slag has no effect on mechanism of hydrothermal synthesizing xonotlite from carbide slag.

4. Conclusions

This paper describes for the first time the preparation of xonotlite using carbide slag as the calcareous material via dynamic hydrothermal synthesis. The SEM and XRD results indicate that pure xonotlite was synthesized successfully from calcined carbide slag. The following conclusions can be drawn:

(1) Different calcination temperatures of the carbide slag have little effect on synthesized xonotlite, but pose big impact on the morphology of secondary particles. Xonotlite slime, prepared by carbide slag calcined at 700 °C and 800 °C, was made up of many large orbicular secondary particles, but xonotlite slime, which was prepared by carbide slag calcined at 900 °C and 1000 °C, was mainly made up of small orbicular secondary particles.
(2) The different pretreatment methods of the carbide slag posed big impact on the crystallinity and morphology of the secondary particles of xonotlite. The calcination of carbide slag is of utmost importance to the synthesis of xonotlite.
(3) Pure xonotlite could be prepared from calcined carbide slag, and small amount of impurities in carbide slag has no effect on the microstructure and morphology of synthesized product.
(4) The process parameters of hydrothermal synthesis of xonotlite synthesized from calcined carbide slag were almost the same as those from pure CaO.
(5) The mechanism of hydrothermal synthesis of xonotlite from carbide slag is the same as that for pure CaO. Therefore, the mechanism of hydrothermal synthesis from carbide slag is not affected by the little amount of impurities.

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