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Alkali-Hydrothermal Synthesis of Acicular Tobermorite Using Natural Mineral K-Feldspar Powder

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This research reports a new economical method of preparing acicular tobermorite as well as high-valuable KOH obtained. Acicular tobermorite was hydrothermally synthesized at 180°C–250°C for 4–8 h using the K-feldspar powder and CaO chemical firstly while the filtrate could be used to prepare KOH. The K-feldspar powder used is from Luonan county of Shaanxi province in China. The XRD analysis indicated that the main phase is microcline with the content of 91%. The chemical analysis showed that the main chemical components of the K-feldspar powder are SiO2 64.53%, Al2O3 16.70% and K2O 14.75% in mass.

The micrographs of the synthesized samples at the condition of different water/solid ratios, hydrothermal treated temperature and time were investigated. It is concluded that the well-crystallized tobermorite was formed with the acicular shape when the synthesized parameters were as follows. nCa/(nSi+nAl) = 0.83, Water/Solid (in mass) = 20, T = 250°C and t = 8 h. The synthesized well-crystalline tobermorite sample was characterized by the use of chemical analysis, powder X-ray diffraction and scanning electron microscope. It is shown that the synthesized sample is acicular with the diameter of around 0.2–0.5 μm.

Keywords K-feldspar; alkali-hydrothermal process; acicular tobermorite; KOH

Introduction

Tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O) was normally synthesized using chemicals of CaO and SiO₂ by hydrothermal process with the chemical reaction as follows.¹⁰⁵

\[
CaO + SiO_2 + H_2O \rightarrow Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O
\]

Tobermorite was used to prepare insulated materials, polymer composite materials and solidify cesium and strontium as well.¹⁶,⁷ Moreover, more than 20% of the Si⁴⁺ ions in the tobermorite crystal could be substituted by Al³⁺ ions.¹ The Al-substituted

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Tobermorite has been prepared using trachyte rock or zeolite by hydrothermal treatment. Amazingly, acicular tobermorite is capable of improving the fracture toughness when it is used for preparing construction or composite materials compared to normal tobermorite.

K-feldspar (KAlSi₃O₈) is a kind of natural aluminosilicate mineral with the main chemical composition of SiO₂ 64.7%, Al₂O₃ 18.4% and K₂O 16.9% which is important potential insoluble potassium resources for preparing potassic salts. It was also used to synthesize microporous and mesoporous materials by hydrothermal treatment or calcination using KOH, Na₂CO₃ or K₂CO₃. K-feldspar is extremely an important raw material for synthesizing tobermorite offering the silica and alumina sources while the filtrated solution could be used for preparing potassic hydroxide as well by the reaction as follows.

\[
6\text{KAlSi}_3\text{O}_8 + 20\text{CaO} + 23\text{H}_2\text{O} \rightarrow 4\text{Ca}_5(\text{Si, Al})_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 6\text{KOH}
\]

This research reported a new economical method of preparing acicular tobermorite as well as high-valuable KOH obtained. Acicular tobermorite was hydrothermally synthesized at 180~250°C for 4~8 h using the K-feldspar powder and CaO chemical while the filtrate could be used to prepare KOH.

**Experiments**

**Chemicals**

The potassium feldspar powder used was from Luonan county of Shaanxi province in China. The XRD analysis indicated that the main phase is microcline with the content of 91%. The chemical analysis results showed that the main components of the K-feldspar powder are SiO₂, Al₂O₃ and K₂O (shown in Table 1). The CaO used is analytical grade reagent and the water was distilled.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN</td>
<td>64.53</td>
<td>0.05</td>
<td>16.70</td>
<td>0.84</td>
<td>0.13</td>
<td>0.56</td>
<td>0.99</td>
<td>0.77</td>
<td>14.75</td>
<td>0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/°C</td>
<td>180~250</td>
</tr>
<tr>
<td>t/h</td>
<td>4~8</td>
</tr>
<tr>
<td>nCa/n(Al+Si)</td>
<td>0.83</td>
</tr>
<tr>
<td>Water/solid (in mass)</td>
<td>10~20</td>
</tr>
<tr>
<td>Stirring speed/r/min</td>
<td>400</td>
</tr>
</tbody>
</table>
Figure 1. SEM images of the synthesized samples.
Instruments

Powder X-ray diffraction (XRD) analysis was performed by D/MAX-RC X-ray diffraction instrument at the condition of $U = 40kV$, $I = 40mA$, $r = 4^\circ/min$, Cu $K_a$ radiation. The micrograph was obtained using KYKY-2800 scanning electron microscope (SEM). The chemical compositions of the samples were determined by wet chemical methods.

Synthesis

The procedures of synthesizing tobermorite using K-feldspar and CaO are as follows. The K-feldspar powder was ball-milled to make the average particle size below 74 $\mu$m. The mixture of the K-feldspar, CaO and distilled water ($nCa/n(Si+Al) = 0.83$, according to the reaction as above) were put into stainless steel autoclave after stirring for 1h. And then the mixture were hydrothermal treated at 180$^\circ$~250$^\circ$ for 4~8 h with the stirring rate of 400 $r/min$. The detailed experimental conditions of synthesizing tobermorite were shown in Table 2. The mixture after hydrothermal treatment was filtrated, washed for 4 times using distilled water and dried at 105$^\circ$C for 24h and the synthesized samples were obtained. The synthesized samples were analyzed by XRD, SEM and chemical analysis finally.

Result and Discussion

Effects of Water/Solids Ratio

The effects of the water/solids ratio (in mass of 10, 15 and 20 respectively) were shown in Table 3 and Figure 1. It is indicated that the synthesized sample is gel-like when the water/solids is 10 that is consistent with the result of Glasser in 2003, C-S-H was formed while the water is insufficient.15 Some acicular tobermorite was observed while the water/solid ratio is increased to 15. However, the most of the solid is still massive particle. The well crystallized tobermorite was synthesized when the water/solid ratio is up to 20 and the synthesized sample is acicular with the diameter of around 0.2~0.5 $\mu$m.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water/solids</th>
<th>$T/^\circ$C</th>
<th>t/h</th>
<th>$r_k$ (%)</th>
<th>Main phase</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG-1</td>
<td>10</td>
<td>250</td>
<td>8</td>
<td>60.7</td>
<td>Tm, P</td>
<td>Gel-like</td>
</tr>
<tr>
<td>LNG-2</td>
<td>15</td>
<td>250</td>
<td>8</td>
<td>74.8</td>
<td>Tm, P</td>
<td>Massive, acicular</td>
</tr>
<tr>
<td>LNG-3</td>
<td>20</td>
<td>250</td>
<td>8</td>
<td>84.3</td>
<td>Tm</td>
<td>Acicular</td>
</tr>
<tr>
<td>LNW-1</td>
<td>20</td>
<td>180</td>
<td>8</td>
<td>53.4</td>
<td>K, Tm, P</td>
<td>Gel-like</td>
</tr>
<tr>
<td>LNW-2</td>
<td>20</td>
<td>220</td>
<td>8</td>
<td>69.7</td>
<td>Tm, P</td>
<td>Massive, acicular</td>
</tr>
<tr>
<td>LNT-1</td>
<td>20</td>
<td>250</td>
<td>4</td>
<td>53.4</td>
<td>K, Tm, P</td>
<td>Massive</td>
</tr>
<tr>
<td>LNT-2</td>
<td>20</td>
<td>250</td>
<td>6</td>
<td>72.8</td>
<td>Tm, P</td>
<td>Acicular</td>
</tr>
</tbody>
</table>

Tm = tobermorite; P = plazolite; K = K-feldspar.
Moreover, the K$_2$O dissolution rate ($r_k$) was more than 84% so that the filtrate would be used for preparing potassium hydroxide or potassic salts.

**Effects of the Treated Temperature**

The effects of the treated temperatures (180°C, 220°C and 250°C) to the synthesized sample were shown in Table 3 and Figure 1. It is indicated that the synthesized sample is still gel-like when $T = 180^\circ$C. Some acicular tobermorite formed while the temperature was up to 220°C. Unfortunately, the solid is the mixture of massive and acicular particles together. The well crystallized tobermorite was obtained when the hydrothermal-treated temperature is 250°C. Simultaneously, the K$_2$O dissolution rate was increased to 84.3% treated at 250°C from 53.4% at 180°C.

**Effects of the Treated Time**

The hydrothermal-treated time is also the key factor to the formation of acicular tobermorite by the results of different times including 4, 6 and 8 h separately shown in Table 3 and Figure 1. Although the acicular solid had been obtained when the treated time was 6h, the second phase still existed in the sample. Therefore, 8h is necessary for the well-crystalline and highly-pure tobermorite.

**Characterization of the Well-Crystalline Tobermorite**

The synthesized tobermorite sample (LNG-3) was characterized by XRD and chemical analysis (Figure 2 and Tables 4 and 5) except for the SEM above.

![Figure 2. XRD patterns of the synthesized tobermorite (LNG-3).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_0$/nm</th>
<th>$b_0$/nm</th>
<th>$c_0$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG-3</td>
<td>0.5593</td>
<td>0.3695</td>
<td>2.2790</td>
</tr>
<tr>
<td>JCPDS (No. 83-1520)</td>
<td>0.5586</td>
<td>0.3696</td>
<td>2.2770</td>
</tr>
</tbody>
</table>
By the result of the chemical analysis, it is known that the synthesized sample was characteristic of lower Si/Ca ratio compared to the theoretical chemical formula Ca₅Si₆O₁₆(OH)₂·4H₂O due to more than 20% Si was substituted by Al in the synthesized tobermorite. The Al source was from the K-feldspar powder. Moreover, 2.73% of K₂O was found in the tobermorite that was consistent to the K₂O dissolution rate of around 84%. It is known that the crystal cell parameters of the tobermorite shown in Table 4 are similar to the JCPDS 83-1520 sample although the synthesized sample’s Si ions were partially substituted by Al ions.

### Conclusions

Acicular tobermorite was hydrothermally synthesized at 180~250°C for 4~8h using the K-feldspar powder and CaO chemical while the filtrate could be used to prepare KOH or potassic salts. The potassium feldspar powder is from Luonan county of Shaanxi province with the main phase of microcline and the K-feldspar content is about 91.4%. The chemical analysis results showed that the main components of the K-feldspar powder were SiO₂ 64.53%, Al₂O₃ 16.70% and K₂O 14.75% in mass.

The morphology of the synthesized samples in the condition of different liquid/solid ratios, hydrothermal treated temperatures and time were studied. It is indicated that the well-crystallized tobermorite was formed with the acicular shape when the synthesized parameters were as follows: \( n\text{Ca}/(n\text{Si}+\text{Al}) = 0.83 \), water/solids = 20, \( T = 250^\circ \text{C} \) and \( t = 8\text{h} \).

The synthesized tobermorite sample was characterized by chemical analysis, X-ray diffraction and SEM. It is shown that the synthesized sample is acicular with the diameter of around 0.2~0.5 μm.

### Acknowledgments

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### Funding

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#### Table 5

Chemical compositions of the synthesized tobermorite (w%) |
<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O⁺</th>
<th>H₂O⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG-3</td>
<td>37.22</td>
<td>0.04</td>
<td>10.14</td>
<td>0.54</td>
<td>0.65</td>
<td>36.31</td>
<td>0.29</td>
<td>2.73</td>
<td>8.72</td>
<td>2.06</td>
</tr>
<tr>
<td>Ce</td>
<td>0.619</td>
<td>0.001</td>
<td>0.199</td>
<td>0.003</td>
<td>0.016</td>
<td>0.647</td>
<td>0.009</td>
<td>0.058</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( C_{\text{ce}} = \) cation coefficient.
References