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Tobermorite synthesis under hydrothermal conditions

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Abstract

The influence of different hydrothermal conditions and starting materials on a preparation of tobermorite was examined. Tobermorite is a mineral, which, thanks to its composition and properties, is an important phase in aerated concrete and it can be also used as an ion exchanger. Tobermorite crystallizes together with other calcium silicate hydrates from the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ during hydrothermal reactions. Paper deals with the key role of starting materials pre-treatment and its influence on the hydrothermal synthesis process. The other important parameters for a synthesis of pure tobermorite as conditions of the reaction, especially the temperature of hydrothermal reaction and curing time were also studied. Phase composition of prepared samples was characterized by XRD and was confirmed by TG-DTA. For overall product characterization, the SEM was used.

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1. Introduction

Tobermorite is a calcium silicate hydrate occurs in nature, where was formed in an alkaline environment under hydrothermal condition. This mineral can be synthesized by hydrothermal reaction in the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system. Until now three tobermorite phases have been distinguished on the basis of their basal spacing: 14 Å tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$) is the most hydrous one, 11 Å tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and water-free 9 Å tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$). [1,2] The most important type is 11 Å tobermorite, which is the major phase found in aerated autoclaved concretes. This building material attracts the attention thanks to its very good heat insulation properties. Typical starting mixture for producing autoclaved aerated concrete consists of lime, quartz sand or coal

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fly ash, cement and gypsum. The morphology and quantity of synthesized tobermorite in this building material can affect his mechanical properties. Thus, to understand the creation of tobermorite during the hydrothermal process is essential. [1,3] The crystal structure of tobermorite also attracts attention because of the similarities with C–S–H phases created during the hydration of Portland cement. [4–6]

The 11 Å tobermorite has a layered structure and the structure model was firstly proposed by Megaw and Kelsey (1956). Despite many experimental studies, a complete description of the structure was not achieved. The problem is to determine the crystal structure of tobermorite from X-ray measurements due to the typical disorder character specific for tobermorite family. Merlino et al. [8,9] successfully applied order-disorder (OD) theory to describe the crystal structure of tobermorite. The structure is build up by a continuous sheet of seven-coordinated calcium atoms. Wollastonite type chains of silicate tetrahedra are attached to both sides of the calcium layer. Depending on the composition of interlayer and degree of hydration, some of neighboring calcium layers can be connected directly by single silicate chains, throughout bridging of interlayer cations and tetrahedral sites. [10] There are two types of 11 Å tobermorite, the so-called 'normal' form, which contain interlayer calcium ions and is able to lose its interlayer water and transforms to 9 Å tobermorite. The second 'anomalous' form is calcium poor analog of 11 Å tobermorite; it does not transform to the 9 Å tobermorite upon dehydration [9,10].

The hydrothermal synthesis of 11 Å tobermorite has been studied by many authors [3,11–27]. Many variable factors have an influence on obtained amount and morphology of synthesized tobermorite particles. The reactivity of silica source is a very important parameter and was extensively studied [3,11–13]. An addition of Al compound to the starting mixture changes also the reaction process. Al³⁺ ions are able to replace silicon in a chain and created an Al-substituted tobermorite [14–21]. This additive speeds up the formation of tobermorite and stabilizes the structure, so no conversion to xonotlite (Ca₆Si₆O₁₇(OH)₂) appears. As another beneficial additive sulfate compounds can be used due to their stabilization properties [22]. The type of a synthetic process is crucial for the synthesis. Most widely the hydrothermal synthesis is used, but different approaches as microwave-assisted synthesis [23,24] or mechanochemical synthesis [25] were also successfully applied.

Although a lot of research has been done in the field of synthesis of tobermorite, until now nobody was able to synthesize a pure form. Pure fully crystallized tobermorite could be then used as a reference material for many fields of chemistry, especially chemistry of building materials. The main purpose of this study was to investigate the influence of various starting materials together with the variable conditions of hydrothermal reaction. Mainly a temperature and a reaction time were examined.

2. Experimental and methods

Four types of silica sources, silica fume Elkem (E), silica fume Grace Davison (G), milled quartz sand (S) and silica sand Dorsilit (D), were used as starting materials. The average particle sizes (d_{50}) of silica sources were 21.11 μm (E), 8.62 μm (G), 28.33 μm (S) and 3.53 μm (D) respectively. Silica sources were mixed with grounded CaCO₃ and pre-treated at 1000 °C for 30 minutes. The CaO/SiO₂ (C/S) ratio was 0.83. This ratio was calculated from the stoichiometric formula for tobermorite, which is 5CaO·6SiO₂·5H₂O. Part of the samples was prepared by mixing silica sand Dorsilit (D) and lime (V) in the same C/S ratio. Water/solid ratio was equal to 2.5 and was the same for all samples.

Hydrothermal reactions were carried out in a Teflon-lined laboratory autoclave placed in a conventional dryer. Prepared slurries were hydrothermally treated at the different reaction temperatures (170–190 °C), autogenous pressures (0.8–1.2 MPa) and the different reaction times (1–10 days). Synthesized products were dried at 60 °C to constant weight.

The phase composition of prepared products (Table 1) was determined by X-ray diffraction analysis (XRD). Data were collected by X-ray diffractometer Empyrean (Pananalytical) using Cu K_α radiation. The morphology of chosen samples was observed by Scanning electron microscopy (SEM, ZEISS EVO LS 10). A thermogravimetric and differential thermal analysis was performed using TG–DTA instrument Q 600 (TA Instruments). Samples were run in Pt crucibles and were heated at 10 °C/min from 20 °C to 1000 °C under the inert argon atmosphere.

Table 1. Reaction conditions and compositions of samples.

Sample	Source of Ca ²⁺	Source of Al ³⁺	Reaction	Reaction
			Temperature (°C)	Time (days)
E170	CaCO ₃	Silica fume Elkem	170	1.5
S170	CaCO ₃	Milled quartz sand	170	1.5
D170	CaCO ₃	Silica sand Dorsilit	170	1.5
G170	CaCO ₃	Silica fume Grace Davison	170	1.5
E190	CaCO ₃	Silica fume Elkem	190	1.5
S190	CaCO ₃	Milled quartz sand	190	1.5
D190	CaCO ₃	Silica sand Dorsilit	190	1.5
G190	CaCO ₃	Silica fume Grace Davison	190	1.5
G1	CaCO ₃	Silica fume Grace Davison	180	1
G3	CaCO ₃	Silica fume Grace Davison	180	3
G5	CaCO ₃	Silica fume Grace Davison	180	5
G10	CaCO ₃	Silica fume Grace Davison	180	10
D1	CaCO ₃	Silica sand Dorsilit	180	1
D3	CaCO ₃	Silica sand Dorsilit	180	3
D5	CaCO ₃	Silica sand Dorsilit	180	5
D10	CaCO ₃	Silica sand Dorsilit	180	10
V1	CaO	Silica sand Dorsilit	180	1
V3	CaO	Silica sand Dorsilit	180	3
V5	CaO	Silica sand Dorsilit	180	5
V10	CaO	Silica sand Dorsilit	180	10

3. Results and discussion

3.1. Effect of temperature and source of SiO₂

Effect of reaction temperature was examined on samples prepared by mixing different silica sources and grounded calcium carbonate. Samples were hydrothermally treated in a Teflon-lined autoclave for 36 hours at temperatures 170 °C and 190 °C. Fig. 1a) shows the XRD patterns of samples prepared at 170 °C and autogenous pressure 0.8 MPa. The main peak for tobermorite is around 8°. It is obvious that tobermorite was prepared in samples where silica fume Grace Davison and silica sand Dorsilit was used, but only as a minor part of a sample. Main crystalline phase in sample S170 is quartz, which means that the temperature was too low for tobermorite formation. The reason is that the applied conditions were not sufficient to proceed the reaction between quartz sand and calcinated calcium carbonate. The same trend is observed in the sample E170. In both samples are observed mostly unreacted phases from starting materials. Almost in all samples the high-temperature phase, wollastonite, was detected. This phase was created during the high temperature pre-treatment of starting mixture before the hydrothermal synthesis. The morphology of powder prepared from silica sand Dorsilit (sample D170) is shown in Fig. 2a). The surface of quartz particles is covered with acicular crystals of tobermorite. Based on XRD analysis there is no tobermorite in the sample S170 prepared from milled quartz sand, as confirmed on SEM image (Fig. 2b)). The morphology of sample S170 is completely different from the sample D170 - no tobermorite acicular crystals are observed, hexagonal crystals of portlandite are present, which were probably created in the reaction of lime with water.

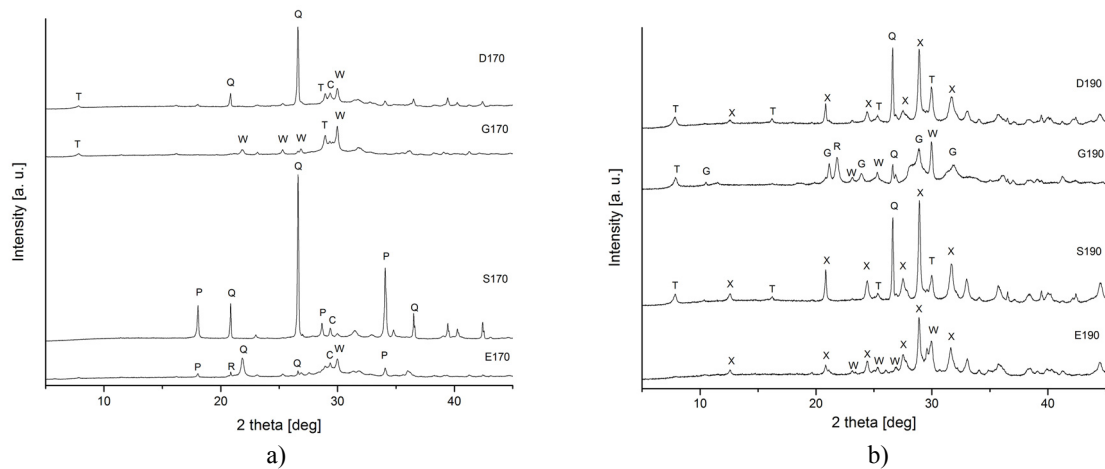


Fig. 1. XRD patterns of samples synthesized at a) 170°C and b) 190 °C. T = tobermorite, Q = quartz, P = portlandite, R = cristobalite, W = wollastonite, C = calcite, X = xonotlite, G = gyrolite.

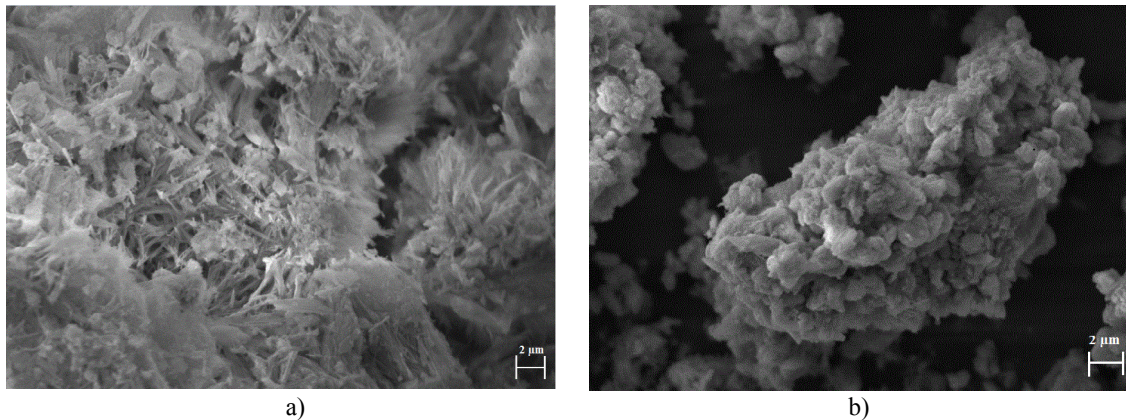


Fig. 2. SEM images of prepared samples at 170 °C using different source of silica a) silica sand Dorsilit (sample D170) and b) specially crushed quartz sand (sample S170).

Fig. 1b) shows samples prepared at 190 °C and autogenous pressure 1.2 MPa. In comparison with samples prepared at 190 °C more new phases were created under the treatment at 190 °C. Tobermorite was determined in all high temperature samples, except sample E190, where instead of tobermorite, xonotlite is created. In sample G190, prepared from silica fume Grace Davison, was created gyrolite. These two minerals are chemically very similar to tobermorite. Gyrolite with chemical formula $\text{Ca}_{16}\text{Si}_{24}\text{O}_{60}(\text{OH})_8 \cdot 12\text{H}_2\text{O}$ is the mineral crystallized from mixture with C/S ratio 0.5–0.6, which is closed to C/S ratio needed for synthesis of tobermorite. Xonotlite is the mineral with formula $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ and can be synthesized from mixture with C/S ratio around 1. It is known that tobermorite is turned into xonotlite after longer reaction time or higher temperatures [26]. The substantial amount of quartz from starting material stayed unreacted, what was also observed in the case of 170 °C. It was proved that the temperature 170 °C is too low for a creation of tobermorite during only 36 hours. The increase in temperature had very important

effect: more new phases were created, but they were created at the expense of the amount of tobermorite. From the data it is obvious that used preparation conditions are not entirely suitable for tobermorite preparation.

3.2. Effect of reaction time

For evaluation of the different reaction time effect, two different silica sources were chosen. From previous results discussed in chapter 3.1., we can say that reactivity of silica source depends mainly on the starting materials particle size. This fact corresponds with the results published by other authors [27,28]. For this reason silica fume Grace Davison and silica sand Dorsilit were used as starting materials. Both are fine grained silica sources with the mean particle size around 5 μm . Based on data discussed previously, the temperature of a synthesis was set to 180 $^{\circ}\text{C}$ with autogenous pressure 1 MPa. This temperature should be high enough for reaction between starting materials, but should prevent transformation of tobermorite to xonotlite. The dependence of reaction time was examined on samples hydrothermally treated for 1, 3, 5 and 10 days.

Fig. 3a) shows XRD patterns for samples prepared using silica sand Dorsilit as a starting material. With the increasing time of a reaction, the amount of synthesized tobermorite slightly decreases at the expense of created xonotlite. Quartz is present in all samples, which means that the C/S ratio is too low for chosen reaction conditions. Low reactivity of silica sand Dorsilit can be also caused by very small particles as was reported by Isu [29]. The results for samples prepared from silica fume Grace Davison are different (Fig. 3b). With the increasing time, the amount of tobermorite significantly increases together with ongoing decreasing amount of quartz. In all samples, the high reactivity of fine silica fume causes creation of wollastonite during pre-treatment and formation of xonotlite, during hydrothermal reaction. Silica fume Grace Davison appears to be too reactive for a synthesis of tobermorite. This fact should be influenced by large surface area of named silica fume.

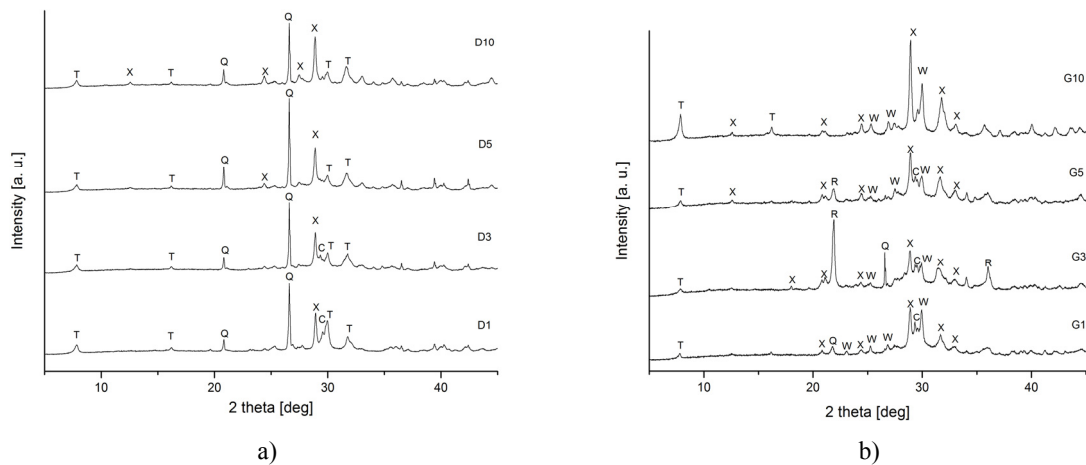


Fig. 3. XRD patterns of samples synthesized for 1-10 days using different silica source a) silica sand Dorsilit and b) silica fume Grace Davison. T = tobermorite, Q = quartz, R = cristobalite, W = wollastonite, C = calcite, X = xonotlite.

3.3. Effect of reaction mixture pre-treatment

High-temperature phases as wollastonite and cristobalite were formed during high temperature pre-treatment of a calcium carbonate mixture and different silica sources. These high temperature phases are not reactive during the hydrothermal reaction, which means that final tobermorite amount significantly decreases. Thus, instead of calcium carbonate, lime was used as a starting material, which eliminated the need of high temperature pre-treatment. Samples were prepared only by mixing lime with silica source and then were hydrothermally treated. From all tested silica sources, silica sand Dorsilit was chosen as the optimal starting material. The reaction

temperature was 180 °C, autogenous pressure 1 MPa and samples were hydrothermally treated for 1, 3, 5 and 10 days.

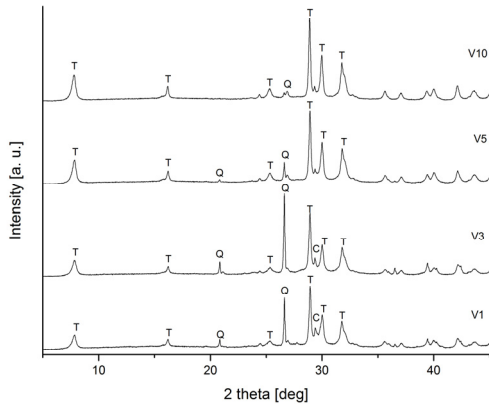


Fig. 4. XRD pattern of samples synthesized for 1-10 days using lime and silica sand Dorsilit. T = tobermorite, Q = quartz, C = calcite.

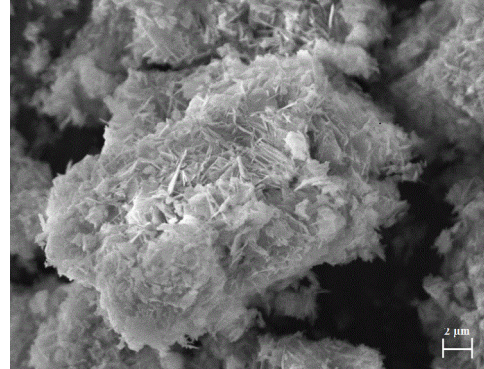


Fig. 5. SEM images of sample prepared from mixture of lime and silica sand Dorsilit, hydrothermally treated for 10 days at 180 °C.

Fig. 4 shows XRD patterns of resulting samples. With the increase of reaction time, the amount of tobermorite rapidly grows. Tobermorite is a major phase of samples, which have gone through hydrothermal reaction for at least 5 days, after which only small amount of quartz remains in prepared samples. Quartz and portlandite need longer curing time to react completely and create pure tobermorite. By C/S ratio shift to higher values the yield of tobermorite synthesis could be improved. Morphology of sample V10 (Fig. 5), shows the sample powder, which is highly agglomerated. The tobermorite formation is confirmed by the presence of acicular crystals, other significant crystal phases were not observed.

3.4. Thermogravimetric analysis

Samples prepared at 180 °C using silica sand Dorsilit as silica source were also analyzed by TG-DTA analysis. Fig. 6 shows measured TG and DTA curves of samples prepared from calcium carbonate or lime as starting materials. The time of the hydrothermal reaction was 1 and 10 days. Tobermorite should lose hydrates type water between 50 °C and 250 °C. Process of the dehydroxylation can be observed on TG curve as a gradual weight loss and on a DTA curve as a broad endothermic peak. Between 250 °C and about 800 °C the remaining molecular water is lost. Tobermorite recrystallizes to wollastonite around 850 °C, which can be also observed on DTA curve as a strong exothermic peak. All presented results are in good agreement with results obtained by Shaw et al [30]. It is obvious that the highest amount of tobermorite was prepared in sample V10. The amount of tobermorite in samples V1 and D1 is comparable. Change in the source of Ca²⁺ species was noticeable after reaction time longer than 1 day.

With the increasing time of hydrothermal reaction, weight loss observed in TG curves of samples D1 and D10 decreases, which indicates lower amount of created tobermorite. These results verify the results obtained by XRD analysis. Also, curves of samples D1 and D10 show small weight loss around 750 °C, which indicate dehydroxylation of xonotlite.

4. Conclusion

Tobermorite was synthesized from different sources of silica and calcium cations. It was proved that silica sources containing smaller particles (around 5 μm) easily participated in the hydrothermal reaction. Together with changing starting materials, the effect of temperature, pressure and time of hydrothermal reaction were examined.

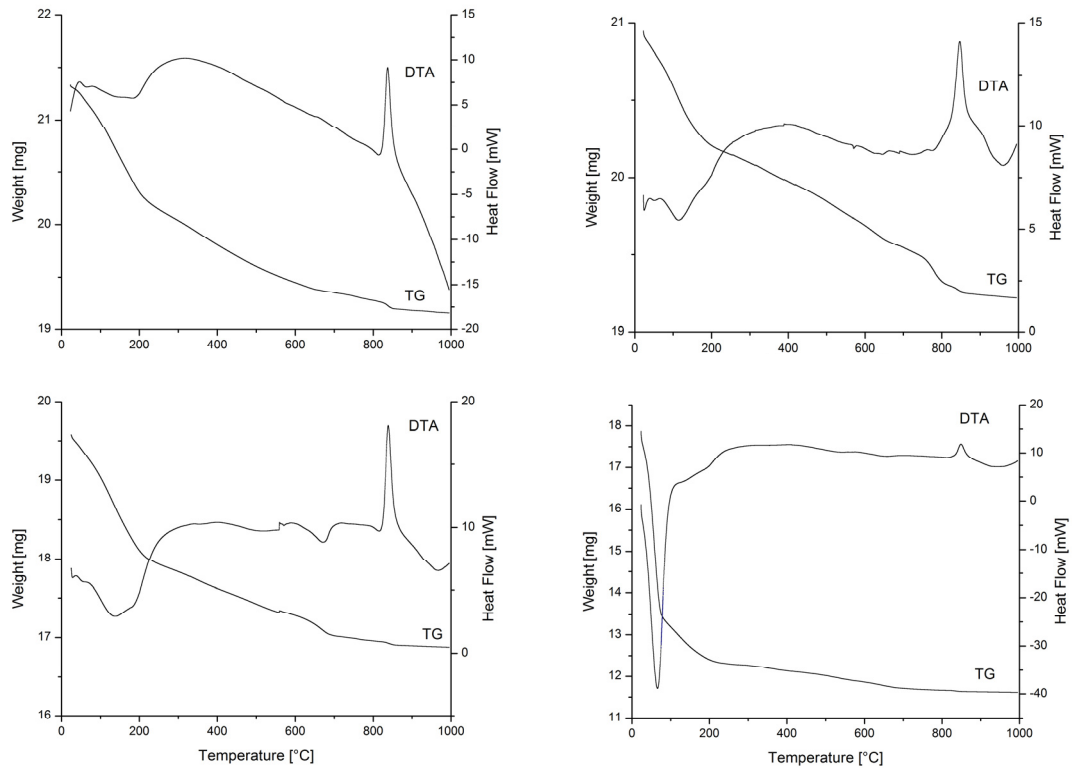


Fig. 6. TG-DTA curves of samples prepared at 180 °C for 1 and 10 days with using silica sand Dorsilit as starting material (from the left top to right site: sample D1, D10, V1 and V10).

The optimal temperature and pressure for the successful synthesis was determined to be 180 °C and 1 MPa. Samples prepared at lower temperatures contained unreacted starting materials. At higher temperature than 180 °C, the formation of undesirable xonotlite instead of desired tobermorite phase occurs. Generally, with the longer reaction time, the tobermorite formation increases. The pre-treatment of a reaction mixture has an important influence on the amount of created tobermorite. Experiments showed, that mineral wollastonite is synthesized during the high temperature pre-treatment of starting materials. During the hydrothermal reaction of the pre-treated mixture, the final amount of tobermorite is lower due to the lower content of Ca^{2+} and Si^{4+} species, which were already consumed throughout the wollastonite formation. The significant influence of Ca^{2+} source was determined. The mixture of silica sand Dorsilit and lime proved to be the optimal starting mixture, where the amount of tobermorite strongly grows with reaction time increase. After five days of the hydrothermal treatment, the tobermorite was observed as the major part. For future research the influence of adjustment of C/S ratio together with different water-to-solid ratio should be studied.

Acknowledgements

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