The Effect of γ-Al₂O₃ Substitution on the Crystallinity of Synthesized Tobermorite from Ultrafine Geothermal Silica

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Abstract

The industrially important cation exchanger tobermorite was synthesized hydrothermally using ultrafine geothermal silica and reagrent grade CaO in an autoclave for 8 hours at 180°C. The γ-Al$_2$O$_3$ was used to substitute 0, 5, 10 and 15% of the silica component in the tobermorite precursors to determine its effect on the crystallinity of the synthesized products. The products of synthesis were then characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Results showed that at 0 to 10% substitution of γ-Al$_2$O$_3$, the crystallinity of the synthesized products was 0%. At 15% substitution, the crystallinity of the synthesized tobermorite was found to increase from 0 to 17.882%. This was observed only after conversion of precursors to C-S-H phases.

Introduction

T obermorite, a group of calcium silica hydrate (C-S-H) minerals, includes a variety of phases with different degrees of crystallinity and variation in composition. Of these, tobermorite with nominal composition $5CaO \cdot 6SiO_2 \cdot 5H_2O$ is highly crystalline, rare and occurs naturally as

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a platy hydrous silicate mineral in calcium silicate rocks. This is referred to as the 1.13-nm tobermorite based on the thickness of elementary layers in its structure. The basic layer consists of a central sheet of calcium and oxygen ions sandwiched by rows of $SiO_2(OH)_2$ tetrahedra that are linked into chains.[1]

Tobermorite itself has a range of Ca/Si from 0.8 to 1.0.[2] Extra Ca fits in the void spaces between silica chains. Al^{3+} ions were found to substitute for the tetrahedral Si atoms in Si-O-Si bridges between chains in tobermorite. This results to formation of cavities which gives potential for ion exchange activities to occur.[3,4] As cation exchanger, applications of tobermorite include water purification, removal of environmental pollutants, analytical and preparative chemistry, nuclear waste treatment, hydrometallurgy, biotechnology, pharmaceuticals and even in food processing.[5,6]

Though naturally rare, tobermorite can be easily synthesized hydrothermally in an autoclave, and the product, being a highly crystalline solid, gives a very strong and highly reproducible XRD pattern.[2] Tobermorite precursors are a mixture of common raw materials such as silica, lime, and argillaceous minerals. The choice of precursors, including particle size and degree of crystallization affect the kinetics and the final phases formed.[7]

Tobermorites were synthesized using quartz samples (particle sizes from sedimentation below 10μm, containing 99.9% SiO_2), colloidal silica, by-product silica (amorphous, 94.4% SiO_2, 10-15μm and converted to cristobalite at 1300°C giving particles <20μm) and silica glass (<10μm, 99.94% SiO_2) at 105-180°C and Ca/(Si+Al) of 0.8 – 1.0 in stirred and unstirred mixtures.[8,9,10] The reactions proceed through the sequence,

$$Ca(OH)_2 + SiO_2 + \gamma\text{-}Al_2O_3 \rightarrow \text{Al-CSH} \rightarrow \text{Al-tobermorite.}$$
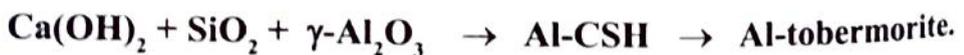
The presence of Al substituting for the Si can accelerate the crystallization of Tobermorite. However, this addition retards the formation of CSH, since γ-alumina decreases the solubility of quartz in the process. Substitution of Al for Si in the tobermorite structure allows 15% replacement before any anomalous behaviors on thermal treatment could occur.[11,12]

It has been established that for synthesis to proceed to formation of tobermorite, silica component should contain around 95% SiO_2 and particle size of < 10 microns. Producing silica with such specific particle size is very difficult and expensive using existing technologies of size reduction

processes. Ultrafine geothermal silica however, is generated locally from the disposal of geothermal effluent. This geothermal silica is presently produced in voluminous amounts at Bacon-Manito geothermal field at Botong, Sorsogon. The silica content is around 98.7% and particle size < 5 microns.[13] Utilizing this waste as a raw material for the development of useful and environment friendly materials seem to be the best alternative to consider. In other words, tobermorite can answer this need.

In the present study, the effect of γ-Al_2O_3 substitution on the crystallinity of synthesized tobermorite from ultrafine geothermal silica will be investigated.

Experimental Procedure

2.1   Characterization and Preparation of Starting Materials

The ultrafine geothermal silica was precipitated from the geothermal effluent. It was then characterized using the Energy Dispersive System (EDS) accessory of the SEM to determine its elemental composition, and XRD to determine its crystallinity. The CaO and γ-alumina used were reagent grade.

The starting materials were individually powdered using mortar and pestle, then proportioned to have Ca/Si+Al ratio of 0.8. Autoclavable vials were used to contain the mixtures. Deionized water was then added to achieve a water to solid ratio equal to 2.0. This was followed by mechanical shaking for 1 minute. The autoclavable vials were then sealed and mixtures were allowed to stand for 12 hours.

2.2   Hydrothermal Treatment

The vials were then unsealed and placed in the autoclave filled with deionized water to one-fourth its total volume. The autoclave was then properly sealed and switched on to start heating. The 180°C setting temperature was achieved after 12 minutes, establishing saturated steam pressure condition. All reactions were done without stirring for 8 hours.

The experimental set-up is shown in Figure 1. After heat treatment,

the autoclave was cooled and the reaction products were filtered using filter paper, washed with deionized water and then dried with ethanol and diethyl ether. Three replicate runs were made.

A. Discharge valve
B. Manometer
C. Safety valve
D. Sample holder
E. Heater
F. Control box
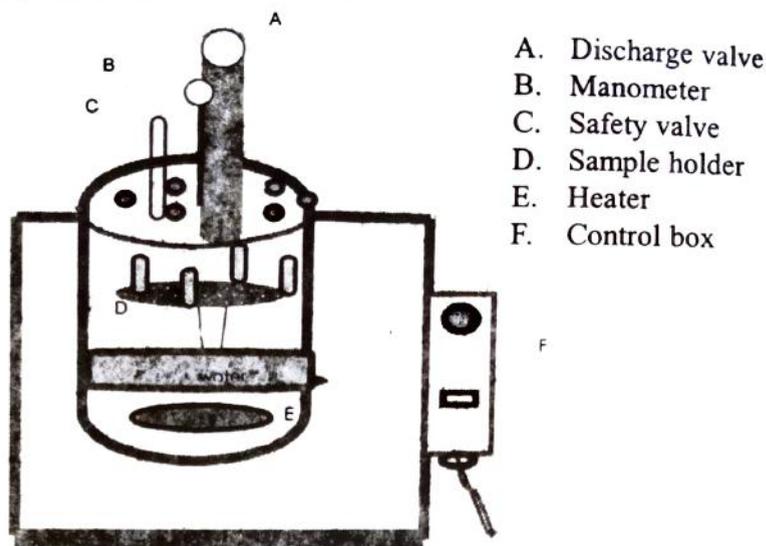
Figure 1. *The Experimental Set-up in the Autoclave.*

2.2 Product Examination

The products of synthesis were first examined using X-ray diffraction. The XRD patterns and corresponding tabulated values for 2θ, d-spacing and relative intensities were generated by a computer with PC-APD diffraction software. With a PC Identify Computer Software, the phases formed were then identified. The results were, however, verified using the Hanawalt method where the computer generated XRD data were matched with the Joint Committee of Powder Diffraction Standard (JCPDS) powder diffraction data.

The corresponding relative intensities of the peaks in the matched patterns were then noted to determine the amount of the phases formed. The data obtained were used in determining the extent of crystallinity according to the method by Alexanderson (1979) [14] where:

$$\% \ Crystallinity = \frac{\% \ Tobermorite}{\% \ Total \ CSH} \ X \ 100. \qquad (1)$$

For simplicity, crystalline tobermorite was referred to the $5CaO \cdot 6SiO_2 \cdot 5H_2O$ tobermorite, while the poorly crystalline tobermorite phases were considered to belong to the C-S-H phases. The poorly crystalline tobermorite phases were however noted to determine the extent of tobermorite conversion from C-S-H. Morphology of the products was examined using a Scanning Electron Microscope.

III. Results and Discussion

3.1   Raw Materials Characterization

SEM-EDS results confirmed that the ultrafine geothermal silica is basically of Si (Figure 2). The generated d-values and relative intensities of the X-ray diffraction peaks compared with the JCPDS data revealed that the geothermal colloidal silica is amorphous (Figure 3). Two low intensity peaks were attributed to minor crystalline impurities present.
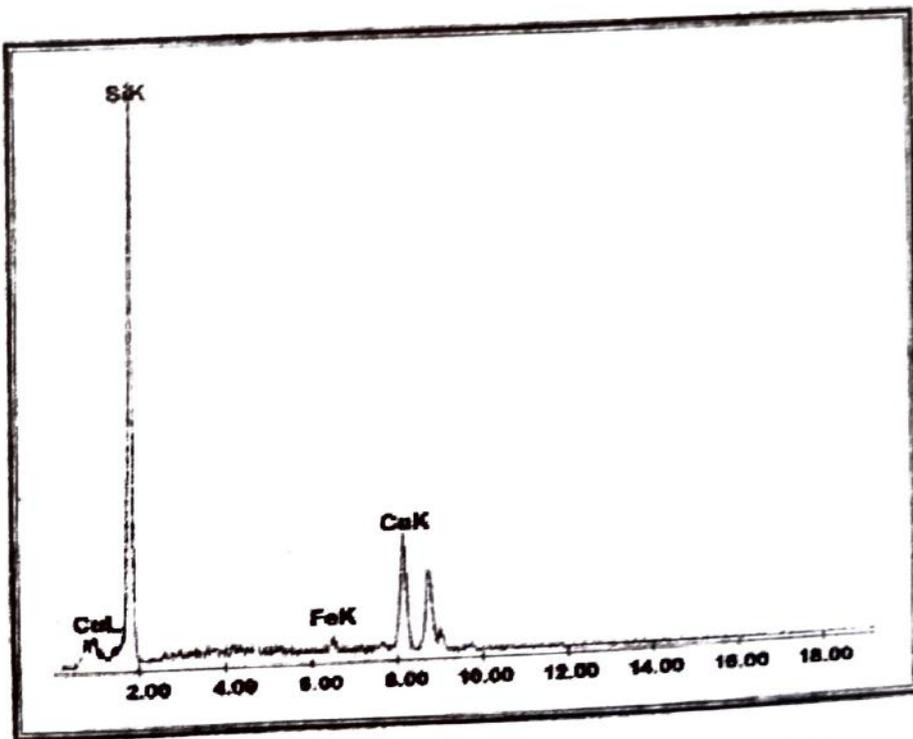
Figure 2. EDS Pattern for Geothermal Colloidal Silica
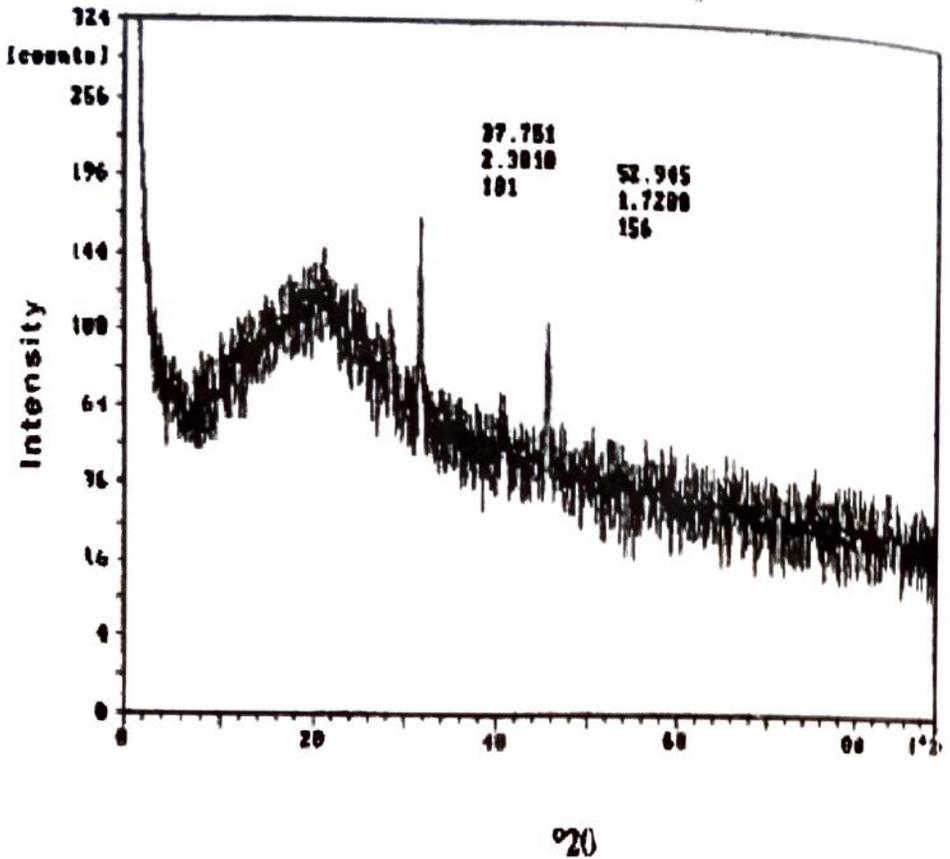
Figure 3. *XRD Pattern of the Geothermal Colloidal Silica*

3.2 XRD Analysis of the Synthesized Products

The XRD results (Figure 4) showed, that crystalline tobermorite phase was only detected in the synthesized product with 15% substitution of γ-Al_2O_3 (D pattern). The characteristic strong intensity lines and corresponding d-spacing matched with the tobermorite XRD pattern for this mixture. The % crystallinity of the synthesized product was determined using equation (1). The average % crystallinity was found to be 17.882%. The other mixtures with 0, 5, and 10% substitution of γ-Al_2O_3 did not reveal any crystalline tobermorite. Other phases detected however, were poorly crystalline tobermorite and the $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (C-S-H) phase (Table 1); both denoted as C in the XRD pattern.
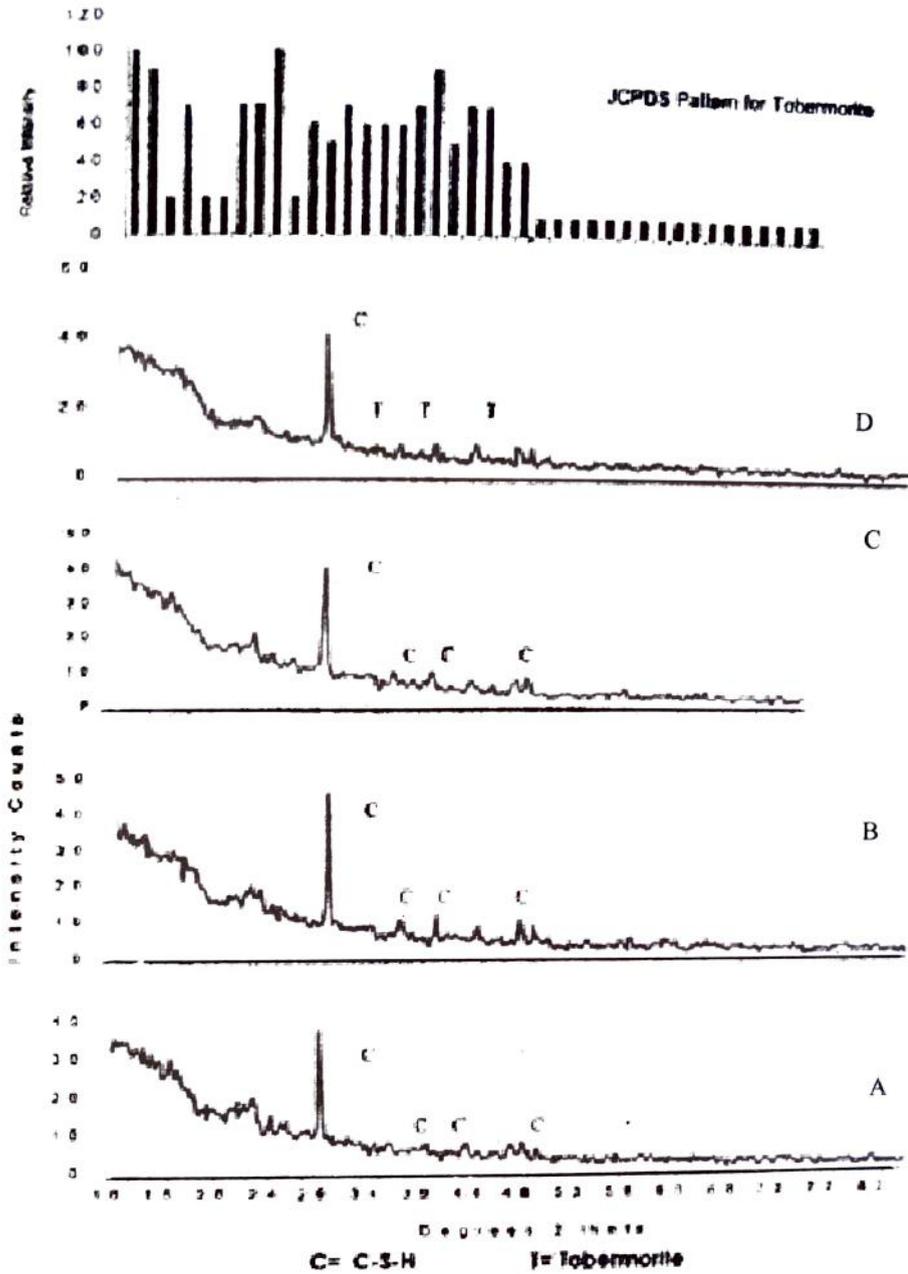
Figure 4. *XRD Pattern of the Synthesized Products*

Table 1. *Mean quantities of phases formed in the synthesized products.*

% γ-Al_2O_3	% Phases Formed		
	C-S-H Phases		Crystalline Tobermorite
	$3CaO \cdot 2SiO_2 \cdot 3H_2O$	Poorly Crystalline Tobermorite	
0	0.00	100.00	0
5	7.349	92.651	0
10	4.721	95.279	0
15	2.494	79.624	17.882

It is evident that at 8 hours of autoclaving, all of the precursors were converted to C-S-H before any crystallization of tobermorite occurred, since there was no traceable unreacted colloidal silica and γ-Al_2O_3 left. The reaction process for this mixture is shown in Figure 5.

CaO, H_2O, Colloidal SiO_2 $\Rightarrow$ C-S-H $\Rightarrow$ Tobermorite + C-S-H (Poorly Crystalline Tobermorite + $3CaO \cdot 2SiO_2 \cdot 3H_2O$)

Figure 5. *The Synthesis Reaction*

Since the colloidal silica was amorphous, at 0 to 10% γ-Al_2O_3 substitution, the mixtures did not convert to crystalline tobermorite perhaps due to the absence of crystalline nuclei around which the $5CaO \cdot 6SiO_2 \cdot 5H_2O$ tobermorite could condense. The amount of γ-Al_2O_3 added was perhaps insufficient for the formation of crystallization nuclei and the 15% substitution was able to promote their formation.

3.3   SEM Results

Figures 6 is the scanning electron micrograph of the raw mix without the addition of γ-alumina. The spherical geothermal colloidal silica can be easily distinguished from the cloud-like CaO. The spherical and cloud-like structures of precursors have been converted to platy tobermorite in Figure 7. Poorly crystalline tobermorite (clusters of fibers) grow at surroundings of the tobermorite plates.
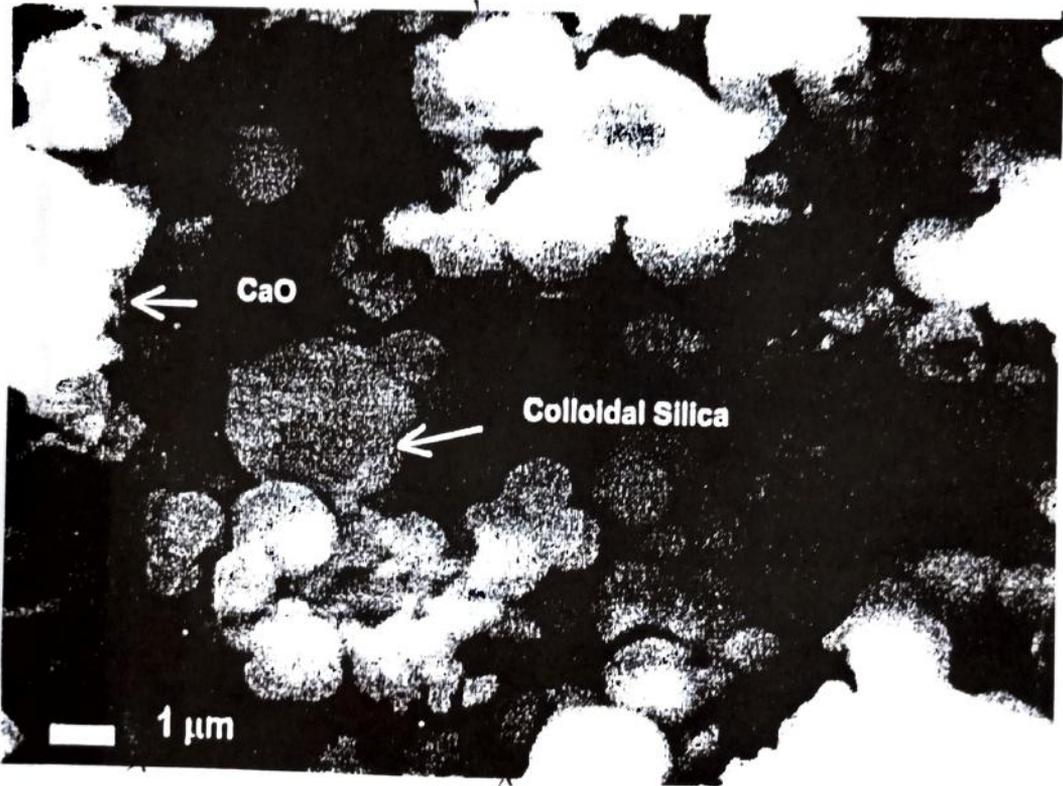
Figure 6. Scanning Electron Micrograph of the Raw Mix
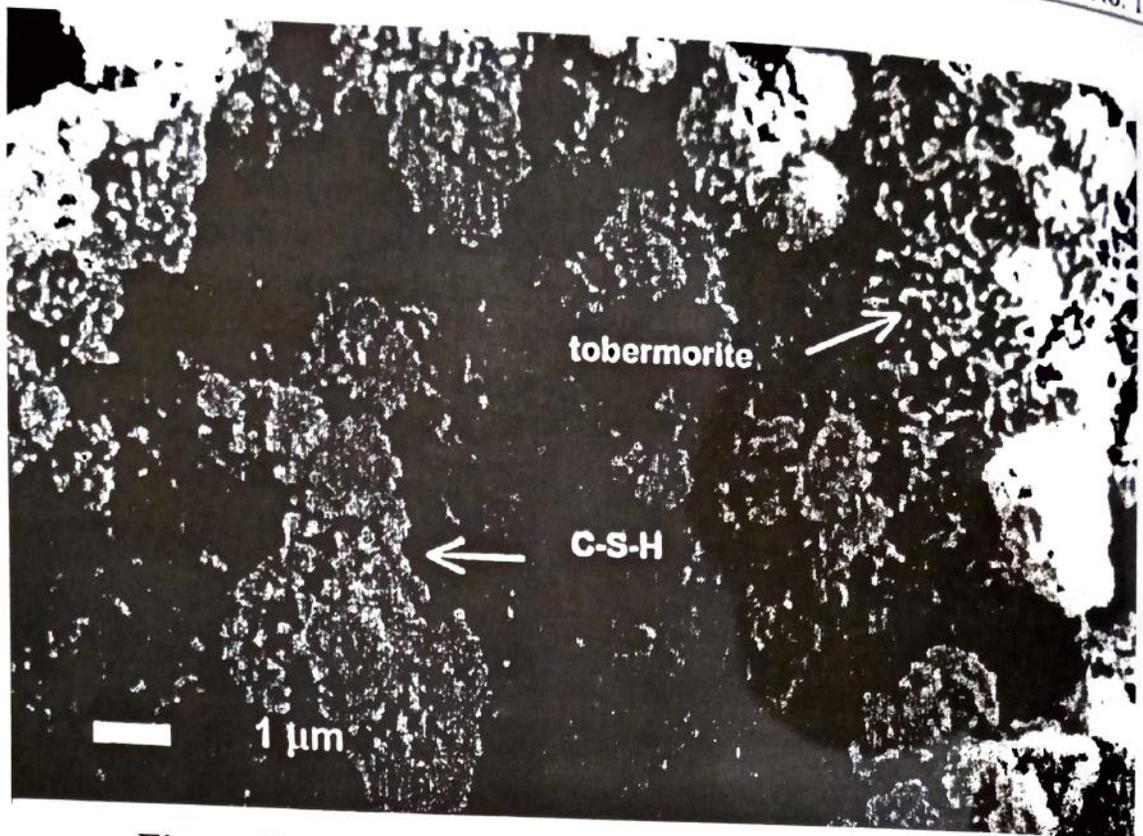
Figure 7. *Scanning Electron Micrograph of the Synthesized Product. (3600x)*

IV. Conclusion

This study therefore concludes that 0 to 10% substitution of γ-Al_2O_3 has no effect on the crystallization of tobermorite. At 15% substitution, the crystallinity of synthesized tobermorite from ultrafine geothermal silica was found to increase. This was observed upon conversion of tobermorite precursors to C-S-H phases.

Acknowledgement

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