SYNTHESIS AND CHARACTERIZATION OF AKERMANITE POWDER

A Thesis in
Mechanical Engineering

by

Caleb A. Zolko

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The thesis of Caleb A. Zolko was reviewed and approved* by the following:

Fariborz Tavangarian  
Assistant Professor of Mechanical Engineering  
Thesis Advisor

Issam Abu-Mahfouz  
Associate Professor of Mechanical Engineering  
Head of the Department of Mechanical Engineering

Richard Ciocci  
Associate Professor of Mechanical Engineering

Amit Banerjee  
Associate Professor of Mechanical Engineering

* Signatures are on file in the Graduate School.
ABSTRACT

Pure Nanocrystallite akermanite powder was synthesized using initial materials: calcium carbonate, magnesium carbonate, and silica. Initial materials were mechanically activated and subsequently annealed at various temperatures. Resultant powders were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) mass spectrometry (MS), X-ray diffractometry (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Results showed that pure nanocrystallite akermanite was synthesized from calcium carbonate, magnesium carbonate, and silica powders mechanically activated for 50 h and subsequently heat treated at 900 °C for 1 h. Nanostructured akermanite had a crystallite size of 67 nm. Additionally, the formation mechanism of akermanite was evaluated. Results showed that akermanite forms through several transition compounds such as enstatite, wollastonite, larnite, and merwinite. Furthermore, pure nanocrystallite akermanite was synthesized via mechanical activation and heat treatment of talc, calcium carbonate, and silica. The formation mechanism was studied. The results showed that akermanite was synthesized through two parallel mechanisms. One was directly, and the other was through the formation and consumption of transitionary compounds. Pure akermanite synthesized through mechanical activation for 20 hours and subsequent heat treatment of 900 °C for 1 h resulted in a crystallite size of 34 nm. Increased mechanical activation or heat treatment had no significant effect on the crystallite structure of akermanite. Mechanical properties of the synthesized akermanite was also evaluated. Akermanite synthesized with 20 h mechanical activation and heat treated at 900 °C for 1 h resulted in a Young’s modulus of 3800 MPa, an ultimate compressive strength of 24.7 MPa, and a density of 2.489 g/cm³.
TABLE OF CONTENTS

LIST OF FIGURES .............................................................................................. v
LIST OF TABLES ................................................................................................. viii
ACKNOWLEDGEMENTS .................................................................................... ix
Chapter 1: Introduction ....................................................................................... 1
Chapter 2: Methodology ....................................................................................... 3
  2.1. Powder preparation .................................................................................... 3
  2.2. Powder characterization ............................................................................ 4
Chapter 3: Synthesis of Akermanite Powder from Calcium Carbonate, Magnesium
Carbonate, and Silica ......................................................................................... 6
  3.1. Simultaneous Thermal Analysis ................................................................. 6
  3.2. X-ray Diffraction Analysis ......................................................................... 7
  3.3. SEM evaluation .......................................................................................... 10
Chapter 4: Synthesis, Characterization and Formation Mechanism of Nanocrystalline
Akermanite Powder ......................................................................................... 12
  4.1. Simultaneous Thermal Analysis ................................................................. 12
  4.2. X-ray Diffraction Analysis ........................................................................ 14
  4.3. Nanostructure evaluation ......................................................................... 17
  4.4. Thermogravimetric analysis/mass spectrometry ..................................... 19
  4.5. The Effect of Mechanical Activation on X-ray Diffraction .................... 20
  4.6. Mechanical evaluation .............................................................................. 23
Chapter 5: Conclusion ......................................................................................... 25
References .......................................................................................................... 26
Appendix A: Figures ............................................................................................ 30
Appendix B: Tables ............................................................................................. 62
LIST OF FIGURES

Fig. 1. TG curves of 1 min and 20 h ball-milled powders .................................................. 30

Fig. 2. DSC curves of 1 min and 20 h ball-milled powders .................................................. 31

Fig. 3. XRD traces of samples ball-milled for 1 min with varying annealing temperatures .................................................................................................................................................................................. 32

Fig. 4. XRD patterns of powder samples ball-milled for 5 h with varying annealing temperatures .................................................................................................................................................................................................................. 33

Fig. 5. XRD traces of samples ball-milled for 10 h annealed at various temperatures .... 34

Fig. 6. XRD patterns of obtained powders from ball-milling for 20 h with varying annealing temperatures .................................................................................................................................................................................................................. 35

Fig. 7. XRD patterns of sample powders milled for 50 h with various annealing temperatures .................................................................................................................................................................................................................. 36

Fig. 8. SEM micrographs of base materials (a,b) calcium carbonate, (c) magnesium carbonate, and (d) silica .................................................................................................................................................................................................................. 37

Fig. 9. SEM micrographs of sample powders ball-milled for 20 h annealed at (a,b) 900 °C and (c,d)1200 °C .................................................................................................................................................................................................................. 38

Fig. 10. STA of 15 min ball milled powder between 20 and 1200 °C ............................... 39

Fig. 11. STA of 20 hour mechanically activated powder from 20 to 1200 °C .............. 40

Fig. 12. X-ray diffraction of powders milled for 15 min and annealed at various temperatures for 1 h .................................................................................................................................................................................................................. 41

Fig. 13. XRD traces of sample powders mechanically activated for 3 h with subsequent annealing of various temperatures .................................................................................................................................................................................................................. 42

Fig. 14. XRD patterns of starting materials milled for 20 h and annealed at various
temperatures.

Fig. 15. XRD traces of powders mechanically activated for 20 h and annealed at 840 °C for various times.

Fig. 16. Crystallite sizes of akermanite calculated via Williamson-Hall method.

Fig. 17. SEM micrographs depicting the morphology of talc (a,b), calcium carbonate (c), and silica (d).

Fig. 18. SEM micrographs of akermanite synthesized from 10 h (a,b) and 20 h (c,d) mechanical activation and heat treated at 900 °C for 1 h.

Fig. 19. TEM micrograph of akermanite synthesized from 20h mechanical activation, with subsequent annealing at 900 °C for 1 h.

Fig. 20. (a) TG and (b) Mass spectrometry of powders after 20h ball milling time.

Fig. 21. XRD traces of unheat treated powders for various ball milling time.

Fig. 22. XRD patterns of powders heat treated at 700 °C ball milled for various times.

Fig. 23. XRD traces of powders heat treated at 800 °C ball milled for varying times.

Fig. 24. XRD patterns of powders obtained from annealing milled powders at 900 °C.

Fig. 25. Mechanical properties of the tablets from the CCS testing.

Fig. S 1 XRD traces of unmilled powdered silica.

Fig. S 2 XRD patterns of base materials milled for 1 h with various annealing temps.

Fig. S 3 XRD patterns of powders milled for 6 h and heat treated at various temps.

Fig. S 4 XRD traces depicting powders ball milled for 10 h with various annealing temps.

Fig. S 5 XRD traces of powders annealed at 500 °C ball milled for various times.

Fig. S 6 XRD traces of powders heat treated at 600 °C with various ball milling times.
Fig. S 7 XRD patterns of powders heat treated at 1000 °C and milled for various times.
LIST OF TABLES

Table 1. Peak angles and their corresponding (h k l) planes, peak heights, full width at half maximum, and particle sizes for akermanite ..........................................................62

Table 2. Average density and porosity of tablets milled for 6, 10, 20, and 50 h. .............................................................................................................................................63
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Chapter 1: Introduction

Akermanite is part of the melilite mineral group of sorosilicates with a chemical formula of \( \text{Ca}_2\text{Mg}_2\text{Si}_2\text{O}_7 \) [1]. It has shown promise within the medical field due to the ability of akermanite to repair bone defects [2]. Akermanite has shown promise as a candidate for use within the body for this purpose due to its bioactivity. Wu et al. [3] evaluated the bioactivity by submerging the ceramic in simulated body fluid (SBF). The surface of the sample formed a hydroxyapatite interface layer following 10 days of being submerged in SBF. In another study, the researchers evaluated akermanite's dissolution and degradation rate [4]. These researchers found that akermanite had a higher dissolution rate than diopside and a lower dissolution rate than bredigite. This results in an increased apatite formation ability and cell proliferation over diopside and bredigite [5]. Akermanite is more effective than \( \beta \)-TCP, diopside, and bredigite at encouraging osteogenesis [2,4,5].

The degradation of akermanite releases \( \text{Ca}^{2+}, \text{Mg}^{2+}, \) and \( \text{Si}^+ \) ions [6]. The release of such ions has been shown to increase osteoblast proliferation, collagen production and encourage bone growth [4, 7-11]. Osteoblast proliferation is significant as it is necessary for bone formation and reabsorption [12]. Loannis et al. [8] studied the dissolution and degradation of bioactive ceramics and the subsequent release of ions. It was shown that Ca ions released, during this process, encourage osteoblast proliferation [8]. Furthermore, it was shown that Si ions have a positive effect on bone metabolism and encourage osteoblast proliferation [8,9]. These results were confirmed by Webster et al. [13] who studied the degradation of akermanite. It was shown that Ca and Si ions, released from the degradation process, encourage osteoblast growth. Zhang et al. [14] determined that Mg ions have a significant effect on osteoblast adhesion and increase the rate of Ca absorption.
The morphology of the surface of akermanite has been shown to have an effect on its bioactivity [14-17]. Akermanite's surface roughness has been shown to enhance osteoblast nodule formation and osteoblast adhesion [15-17]. This effect is significant due to how osteoblast adhesion is required for bone growth [16]. This is further proven by Xiaoni et al. [18] who evaluated the effect of akermanite’s surface morphology and showed that increasing the surface roughness results in improved apatite formation ability.

Akermanite can be synthesized through various methods. Combustion synthesis involves the combustion of metal nitrate and urea [18]. Bhatkar et al. [19] used this method to synthesize akermanite, however, the resultant akermanite was doped with Eu^{2+} due to the nature of the combustion process. The sintering method is another technique of synthesizing akermanite [20]. This method heats the ceramic causing it to undergo substantial grain growth which results in the increased size of the crystallite structure. Ventura et al. [21] used this method to produce their akermanite. However, the produced akermanite had an amorphous structure along with impurities. The sol-gel method is another common method in which akermanite can be synthesized [21-23]. This method is expensive due to the cost of the required initial materials. It also requires close attention to be paid to the time expensive processes involved [23].

Nanocrystallite akermanite was synthesized using the ball milling technique. Ball milling is an easy to use, safe, and economical method for synthesizing akermanite. Akermanite was synthesized from magnesium carbonate, calcium carbonate, and silica powders. Additionally, the formation mechanism of akermanite was evaluated. Due to this technique the formation of akermanite was achieved at a much lower temperature compared to a previously reported study [24].
Chapter 2: Methodology

2.1. Powder preparation

Calcium carbonate (CaCO$_3$) (99% purity, Acros Organics), magnesium carbonate (MgCO$_3$) (99% purity, Acros Organics), and silicate (SiO$_2$) (99% purity, Sigma-Aldrich) powders were the base ingredients. Calcium carbonate, magnesium carbonate, and silicate were mixed in a molar ratio of 2:1:2. This powder was milled in a planetary ball mill (Tencan, Model XQM-1-A) at a speed of 500 rpm. A zirconia milling container with 5 large, 10 medium, 10 small (10mm, 5mm, 2mm, respectively) zirconia milling balls were used. A weight ratio of 10:1 of ball to powder was used in every run of the planetary ball mill. Powders were ball milled up to 20 h. The ball mill samples were heat treated from 700 to 1200 °C for 1 h within a SX2-2-18TP Xinkyo furnace.

Additionally, Talc, (Mg$_3$Si$_4$O$_{10}$(OH)$_2$) (99% purity, Sigma-Aldrich), Calcium carbonate (CaCO$_3$) (99% purity, Acros Organics), and silicate (SiO$_2$) (99% purity, Sigma-Aldrich) powders were used as the initial materials. Talc, Calcium carbonate, and silicate were mixed in a molar ratio of 1:6:2. The mixed powder was milled using a planetary ball mill (Tencan, model XQM-1-A) with the rotational speed of the main disc equal to 500 rpm. Zirconia milling container and balls 10mm, 5mm, and 2mm were used in a ratio of 5:10:10. A ball to powder weight ratio was adjusted to 10:1. The powders were ball milled for 15 min, 1, 3, 6, 10, 15, and 20 h. The ball mill samples were heat treated at 500, 600, 700, 800, 900, and 1000 °C for 1 hour within a SX2-2-18TP Xinkyo with a heating/cooling rate of 10 °C/min. Akermanite powders were pressed into tablets of height one cm and a diameter of one cm. These tablets were prepared with powders milled for 6, 10, 20, and 50 h. Tablets were pressed with a pressure of 100 MPa and subsequently annealed at 1200 °C.
for 5h.

2.2. Powder characterization

X-ray diffractometry (XRD) technique was used on both the initial powders and ball milled samples after heat treatment. This test was performed using a PANalytical Empyrean diffractometer with Cu Kα radiation ($\lambda=0.154056$ nm). XRD was performed in the 2θ range of 20-80° utilizing a step size of 0.026° along with a time step of 30.6 s. Crystallite sizes were calculated using the XRD results in conjunction with the Williamson-Hall method [25].

$$\beta \cos \theta = \frac{K\lambda}{D} + \epsilon \sin \theta$$  \hspace{1cm} (2-1)

Where $\beta$ is the full width at half maximum height of the peak, $\theta$ is the Bragg diffraction angle, $K$ is the Scherrer constant (.91), $\lambda$ is the wavelength of the radiation used in the XRD test, $D$ is the crystallite size, and $\epsilon$ is the average internal strain.

To study the morphology of akermanite, scanning electron microscopy (SEM) was performed with a Helios Nanolab 660. SEM was performed utilizing an acceleration voltage in between 3 to 20kV. Results from SEM were used with ImageJ software to determine the particle sizes of akermanite. Simultaneous thermal analysis (STA) was performed with an SDT Q600 on milled powders to observe any exothermic peaks. Any such peak may indicate the crystallization temperature of akermanite. Thermogravimetry (TG) was performed on milled powders to determine the magnitude of weight losses, during heat treatment, and their related temperatures. TG was also performed to determine what materials are released from the system. Using the Discovery Series TGA5500 machine, this test was performed for up to 1200 °C under nitrogen gas flow and at a heating
rate of 10 °C/min. Transmission electron microscopy (TEM) was performed on akermanite samples to evaluate the crystallography of the akermanite powders, utilizing a FEI Talos.

Mechanical properties of akermanite tablets were evaluated. Cold crush testing was performed on tablets using an MTS Insight (Electromechanical – 30kN Standard Length). Aluminum anvils were used. Density and porosity of the tablets were also evaluated using a DahoMeter DE-120M densimeter. The apparent porosity was calculated utilizing the following equations [26].

Bulk density = D/(W-S) \hspace{1cm} (2-2)

Apparent porosity = (W-D)/(W-S) \hspace{1cm} (2-3)

Where D is the dry weight of the tablet, W is the wet weight, and S is the suspended wet weight of the tablet in water.
Chapter 3: Synthesis of Akermanite Powder from Calcium Carbonate, Magnesium Carbonate, and Silica

3.1 Simultaneous Thermal Analysis

STA testing was utilized to study powders mechanically activated for 1 min and 20 h. Fig. 1 shows the thermogravimetry (TG) curve of the mechanically activated powders. Additionally, Fig. 2 depicts the differential scanning calorimetry (DSC) trace of the ball milled powders.

Increasing the milling time from 1 min to 20 h changes several characteristics of the TG curve. With only one min milling time, powders did not have a substantial weight loss step until 350-450 °C. The majority of this weight loss could be attributed to the evaporation of the absorbed water as well as the decomposition of magnesium carbonate [27, 28]. After increasing ball milling time to 20 h the weight loss step shifts to 65-200 °C. Additionally, the second weight loss step has a similar effect. The decomposition of calcium carbonate could be attributed to the second step which occurs at 600-740 °C [29].

Increasing the milling time to 20 h ball milling, the weight loss step shifts to 440-700 °C. With increased mechanical activation, the weight loss steps occurred at decreased temperatures. This could be due to the effect of mechanical activation on the powder. Mechanically activating the powder decreases the crystallinity as well as crushing the particles into smaller sizes, which has the effect of volatile materials leaving the system with less energy. Other researchers noticed this phenomenon while studying the effect of mechanical activation on TG curves [30].

The DSC curves of 1 min mechanically activated powder depicted endothermic peaks at 210, 400 and 730 °C, which can be attributed to the release of absorbed water and
decomposition of both carbonates [27-29]. The exothermic peak that occurs at 900 °C was
due to the formation of akermanite [31,32]. After 20 h of mechanical activation, the
intensity of the exothermic peak increases while shifting to a lower temperature (875 °C)
which can be attributed to the faster formation of akermanite due to the increased kinetics
of the reaction [33].

3.2 X-ray Diffraction Analysis

XRD testing was performed on the mechanically activated and heat-treated
powders for the purpose of characterizing them. Powders were mechanically activated for
1 min, 5, 10, and 20 h. Mechanically activated powders were subsequently heat treated
from 700 to 1200 °C for 1 hr.

Fig. 3 depicts the XRD traces of powder mechanically activated for 1 min with
various annealing temperatures. SiO₂ (Silica) powder was not shown on XRD traces, which
can be seen in Fig. S1. After heat treating powders at 700 °C, MgCO₃ (magnesite)
completely decomposes into MgO (Magnesia) (XRD JCPDS data file No. 00-004-0829)
[34]. According to this fact, the initial reaction was the decomposition of magnesite, which
occurred according to the following reaction:

\[ MgCO₃ \rightarrow MgO + CO₂ \]  \hspace{1cm} (1)

Weight loss, of powder mechanically activated for 1 min, between 350 - 450 °C, shown in
Fig. 1, can be attributed to the calcination of magnesite [27].

CaCO₃ (Calcite) (XRD JCPDS data file No. 00-005-0586) did not completely
decompose by 700 °C. Abdolmohammadi et al. [29] determined that CaCO₃ begins
decomposition at approximately 650 °C. However, the time and temperature was not
enough to completely decompose calcite at this temperature. By increasing the temperature to 800 °C, CaCO\textsubscript{3} finished its decomposition into CaO (calcia) (XRD JCPDS data file No. 00-037-1497) according to the following reaction [35].

\[
CaCO_3 \rightarrow CaO + CO_2
\]  

(2)

The weight loss, of 1 min ball milled powder, between 600 - 740 °C, shown in Fig. 1, can be attributed to this reaction. After increasing the temperature to 1200 °C, only a small peak of akermanite was characterized in the XRD pattern, as can be seen in Fig. 3. Transition phases of enstatite, wollastonite, larnite, and merwinitne are shown in the XRD traces between 900 and 1200 °C.

The XRD traces of the powder mechanically activated for 5 h with various heat treatment temperatures can be seen in Fig. 2. Initial materials and their decompositions have smaller peaks. This phenomenon may be due to the induced stresses, deformation and resultant amorphous structure which was caused by the mechanical activation on the powder [36]. By 900 °C, the phase CaSiO\textsubscript{3} (Wollastonite) (XRD JCPDS data file No. 00-010-0489) began to synthesize, and the reaction and can be expressed as follows [37, 38].

\[
CaO + SiO_2 \rightarrow CaSiO_3
\]  

(3)

Additionally, another phase that began to form at 900 °C is MgSiO\textsubscript{3} (enstatite) (XRD JCPDS data file No. 00-003-0520). Shon et al. [39] showed that MgO and SiO\textsubscript{2} react to form MgSiO\textsubscript{3} in the following manner:

\[
MgO + SiO_2 \rightarrow MgSiO_3
\]  

(4)

By increasing the temperature to 1000 °C, calcia and Wollastonite began to react together synthesizing Ca\textsubscript{2}SiO\textsubscript{4} (larnite) (XRD JCPDS data file No. 00-002-0866) [40, 41]. Therefore, the next reaction is as follows:
\[ CaSiO_3 + CaO \rightarrow Ca_2SiO_4 \]  \hspace{1cm} (5)

Fig. 5 depicts the XRD traces of powder mechanically activated for 10 h with various sintering temperatures. Calcite and calcia were no longer observed on the XRD traces. By 800 °C \( Ca_3Mg(SiO_4)_2 \) (merwinite) (XRD JCPDS data file No. 00-025-0161) begins to form. Merwinite is formed through the reactions between \( Ca_2SiO_4, \) CaO, and MgSiO_3 as follows [42,43].

\[ Ca_2SiO_4 + CaO + MgSiO_3 \rightarrow Ca_3Mg(SiO_4)_2 \]  \hspace{1cm} (6)

Increasing the annealing temperature, the characteristic peaks of merwinite grow in intensity.

Fig. 6 shows the XRD patterns of powder mechanically activated for 20 h with varying annealing temperatures. \( Ca_2MgSi_2O_7 \) (akermanite) (XRD JCPDS data file No. 01-077-1149) began to form after powders undergo heat treatment at 800 °C. The final reaction of akermanite formation occurred through the reaction between merwinite, enstatite, and Silica as follows:

\[ 2Ca_3Mg(SiO_4)_2 + MgSiO_3 + SiO_2 \rightarrow 3Ca_2MgSi_2O_7 \]  \hspace{1cm} (7)

The synthesis of akermanite was finished by 900 °C. There were no secondary phases present. Further increasing the heat treatment temperature did not have an effect on the XRD traces.

Initial materials and the decompositions did not show on XRD traces related to high mechanical activation time. This was due to the fact that mechanical activation degrades the crystal structure of the particles [36]. The reactions related to the formation of akermanite were diffusion-based. This results in long reaction times. Zanetti et al. [25] was able to synthesize akermanite by annealing tablets of base materials at a temperature of 950
°C for 48 h for an initial cycle with two to three additional cycles at 1300 °C for 48 h to achieve pure akermanite. With the same base materials, pure akermanite was able to be produced with only a single heat treatment cycle at 900 °C for 1 h. This drastic change to the kinetic and thermodynamic can be attributed to several benefits related to the mechanical activation of the powder. By mechanically activating the powder, the particles were reduced in size which result in smaller diffusion paths, increased vacancies, increased dislocations, and grain boundaries which are able to enhance the diffusion rate of the reaction [44].

Mechanical activation of 50 h can be seen in the XRD traces shown in Fig. 7. There were not any significant changes that occur between 20 and 50 h of mechanical activation. Crystallite sizes of akermanite, synthesized through 20 and 50 h of mechanical activation with subsequent annealing at 900 °C for 1 h, were calculated through the Williamson-hall technique [26]. Table 1 depicts the hkl plane, peak height, full width at half maximum, as well as the crystallite sizes from akermanite that was synthesized from 50 h. Average crystallite size for akermanite was calculated to be 67nm. Additionally, the crystallite size of akermanite synthesized from 20 h of milling was calculated to be 142 nm.

3.3 SEM evaluation

SEM was utilized to characterize both the base materials and annealed akermanite powders. Fig. 8 depicts the surface morphology of calcium carbonate (a,b), magnesium carbonate (c) and silica (d). The calcium carbonate particles were shown to be thin rods with a length up to 1 µm. Additionally, magnesium carbonate was shown to be round particles made up of thin sheets that are sintered together, with sizes of 50 and 2 µm,
respectively. Silica particles were shown to be round and are porous with a size of 10 µm.

Fig. 9 shows the SEM micrographs of akermanite synthesized from 20 h mechanical activation with subsequent annealing at various temperatures. Akermanite particles were shown to be round and have been sintered together, forming macroporous structures (Fig. 9d). These particles had a mean size of approximately 40 µm. Akermanite particles that were annealed at 900 °C were determined to be between 25 nm and 500 nm. Particles that were heat treated at 1200 °C, shown in Fig. 9 c and d, are more consistent in their size which ranged between 100 and 500 nm. However, these particles were shown to be more significantly sintered together than their lower temperature counterparts. This was due to the effect of the higher annealing temperature. The crystallite sizes of powders mechanically activated for 20 and 50 h and subsequently annealed at 900 °C were calculated to be 142 and 67 nm. Therefore, particles of akermanite were numerous nanocrystallites that have agglomerated together to form larger particles.
Talc, a material used in baby powder, is an extraordinarily soft mineral. This mineral is also found in abundance resulting in it being inexpensive. Due to this fact, talc allows for a less expensive system, and its softness will result in less wear on the planetary ball mill. Not only will Talc ($\text{Mg}_3\text{SiO}_10\text{(OH)}_2$) be replacing MgCO$_3$ as the Mg source for the new system, it will also provide some of the required Si. CaCO$_3$ will remain as the sole Ca source of the system. Additionally, SiO$_2$ will be used as the remainder of the Si source. It is expected that the Talc system will be able to produce nanocrystallite akermanite at a faster rate and with a smaller resultant crystallite size.

4.1 Simultaneous Thermal Analysis

STA was utilized to characterize powders mechanically activated for 15 minutes and 20 hours. Fig. 10 depicts the thermogravimetry (TG) and differential scanning calorimetry (DSC) of powder mechanically activated for 15 min and annealed from $20^\circ\text{C}$ to $1200^\circ\text{C}$. The TG showed only a single weight loss step that occurs between $650^\circ\text{C}$ and $770^\circ\text{C}$. The DSC trace depicted a single endothermic peak that occurs at $760^\circ\text{C}$. Talc and calcium carbonate decompose during heat treatment which results in a weight loss. Talc ($\text{Mg}_3\text{SiO}_10\text{(OH)}_2$) will release structural $\text{H}_2\text{O}$ during the decomposition [45]. Calcium carbonate's decomposition, which has been well studied, releases $\text{CO}_2$ [35]. During the decomposition process, the base materials should theoretically have a weight loss of 25.6% [29, 45]. However, 15 min and 20 h mechanically activated powders both show an experimental weight loss of 27%. The difference could be due to atmospheric water, that
was absorbed, being released [28, 29].

Fig. 11 depicts the TG and DSC of powders that were mechanically activated for 20 h. The TG depicted two steps of weight loss. The initial step can be described as having two parts. The first part of the weight loss step begins at 300 °C and finishes at 560 °C. Additionally, the second part of the weight loss begins at 560 °C and finishes by 675 °C. The second weight loss step, of the system, starts at 780 °C and finishes by 840 °C. The DSC trace depicts two peaks, which were related to reactions. The first of these peaks was a small endothermic peak which occurred at 640 °C. The second peak, which was a significant exothermic peak occurred at 840 °C.

Increasing the mechanical activation time of the powders, from 15 min to 20 h, the TG and DSC traces changed significantly. The change in the TG was a gain of a second weight loss step. By increasing the mechanical activation, the weight loss shifted from 550-770 °C to 300-675 °C. Additionally, another weight loss step occurred at 780-840 °C. This addition to the system might be due to the increased mechanical activation. This was supported by other researchers who have studied the effect of mechanical activation on TG. These researchers have determined that mechanical activation can have an effect the locations, number, and slope of TG weight loss steps [30]. By increasing the mechanical activation time there was also a shift of the endothermic peak from 760 °C to 640 °C. On the DSC trace for powders that were mechanically activated for 20h, there was an exothermic peak that occurs at 840 °C. This exothermic peak may be a result of the synthesis of akermanite [32].
4.2 X-ray Diffraction Analysis

X-ray diffraction (XRD) testing was used on powders that were mechanically activated and annealed. XRD was used to characterize these powders. The base materials were mechanically activated for 15 min, 1, 3, 6, 10, 20 h. They were then subsequently annealed at various temperatures between 500 and 1000 °C. The XRD traces of powder mechanically activated for 15 min, with various annealing temperatures, are shown in Fig. 12. Although, talc (XRD JCPDS data file No. 00-013-0558) and CaCO₃ (Calcite) (XRD JCPDS data file No. 00-005-0586) are visible in the XRD traces, silica was not visible on the traces. This fact was confirmed by the XRD trace of silica powder, which can be seen in Fig. S1. Calcite almost completely decomposed into CaO (calcia) (XRD JCPDS data file No. 00-037-1497) and CO₂ by 800 °C. This occurred according to the following reaction [35].

\[
CaCO_3 \rightarrow CaO + CO_2 \quad (8)
\]

The cause of the weight loss shown in Fig. 1, between 650 °C and 770 °C, was due to the decomposition of calcite. Additionally, talc completely decomposes by 1000 °C. This decomposition resulted in the formation of MgSiO₃ (enstatite) (XRD JCPDS data file No. 00-003-0520), SiO₂, and H₂O according to the following equation [45].

\[
Mg_3SiO_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O \quad (9)
\]

Although enstatite was visible by 900 °C, by 1000 °C there were only minor peaks that remain. The transition phases of enstatite, larnite, wollastonite, and merwinite were dominant within the traces of 900 and 1000 °C. Akermanite could not finish synthesizing by 1000 °C, and only minor peaks of akermanite were visible. Additional mechanical activation of 1 h had no significant changes on the traces. This fact can be observed in Fig.
The XRD patterns of powders mechanically activated for 3 h and subsequently annealed at various temperatures are shown in Fig. 13. Due to the increased mechanical activation, the decompositions of talc and calcite accelerated and occurred before 800 °C. An additional effect of the increased mechanical activation was that calcia was no longer clearly shown within the trace. This was due to the significant deformation to the crystal structure from the mechanical activation [42]. By 900 °C, akermanite becomes the dominant phase in the XRD trace. Increasing the temperature to 1000 °C did not finish the synthesis of akermanite. Transitionary phases were still visible. Further increasing mechanical activation to 6 and 10 h, which can be seen in Fig S3 and S4 respectively, only had a minor effect on reducing the secondary phases shown in the traces of 900 and 1000 °C. Akermanite still was not able to be completely synthesized.

The XRD traces of materials that were mechanically activated for 20 h with various annealing temperatures are shown in Fig. 14. With the increased mechanical activation, talc and calcite were still visible from 500 to 800 °C. However, their decomposition and transitional phases were not visible at this point. By 900 °C, pure akermanite had finished synthesizing. There were no secondary phases present. Although in powder mechanically activated for 15 min, akermanite was able to begin synthesizing at 900°C it was unable to finish. By increasing the mechanical activation to 20 h the kinetics of the system had advanced sufficiently so that pure akermanite was able to finish synthesis at 900 and 1000 °C [36]. The kinetics of the system changing, due to the mechanical activation of the powder, could be due to the fact that the synthesis of akermanite is a diffusion-based reaction [44]. Mechanical activation had the effect of crushing the particles of the powders
which results in shortened diffusion paths. The process also had the effect of creating a more homogeneous powder.

Due to the fact that there is an exothermic peak, shown in Fig. 10, at 840 °C an evaluation was performed on powders that were mechanically activated for 20 h with subsequent annealing at 840 °C for various holding times. Fig. 15 shows the XRD traces of this evaluation. Only peaks that were related to talc and calcite are visible at 0 min hold time. However, further increasing the hold time to 5 h showed peaks related to Ca$_2$MgSi$_2$O$_7$ (akermanite) (XRD JCPDS data file No. 01-077-1149). Due to this fact, the first step that follows the decomposition of the initial materials was the direct reaction of these decompositions. This reaction of the synthesis of akermanite was as follows.

\[
2\text{CaO} + \text{MgSi}_3\text{O}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{MgSi}_2\text{O}_7
\]  

(10)

Further increasing the holding time to 7.5 h showed an increase in the peaks related to akermanite. Additionally, the trace showed the growth of a new secondary phases including enstatite, which is a result of the decomposition of talc. CaSiO$_3$ (Wollastonite) (XRD JCPDS data file No. 00-010-0489) was the next phase that begins to appear. Wollastonite was created through the reactions between calcia and silica which can be described according to the following equation [37].

\[
\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3
\]  

(11)

Wollastonite subsequently reacted with calcia and forms Ca$_2$SiO$_4$ (larnite) (XRD JCPDS data file No. 00-002-0866) according to the following formula [40, 41].

\[
\text{CaSiO}_3 + \text{CaO} \rightarrow \text{Ca}_2\text{SiO}_4
\]  

(12)

The final phase that was forming within the sample was Ca$_3$Mg(SiO$_4$)$_2$ (merwinite) (XRD JCPDS data file No. 00-025-0161). Merwinite formed through the reaction of larnite,
calcia, and enstatite according to the following formula [43].

\[ Ca_2SiO_4 + CaO + MgSiO_3 \rightarrow Ca_3Mg(SiO_4)_2 \]  

(13)

Further increasing the hold time of the powders to 15 h resulted in the transition phases being consumed in the final reaction of the system. Merwinite, enstatite, and silica reacted together forming akermanite according to the following reaction.

\[ 2Ca_3Mg(SiO_4)_2 + MgSiO_3 + SiO_2 \rightarrow 3Ca_2MgSi_2O_7 \]  

(14)

This final reaction consumed all base materials and transition compounds. These results showed that there were two separate mechanisms that were within the synthesis of akermanite. Reactions related to the synthesis of akermanite occurred both directly and indirectly through transition compounds simultaneously. Additionally, the results showed that akermanite was able to begin synthesizing at 840 °C, the lowest reported temperature. The peaks in the XRD shift according to hold time. This could be due to the reduction of the strain, induced by the mechanical activation, within the crystal structure [46].

Williamson-Hall method was used, in conjunction with XRD results, to evaluate the crystallite sizes of akermanite [25]. These results are shown within Fig. 16. The sizes of the crystallites range between 21 and 44 nm. Crystallite size was shown to be affected by mechanical activation as well as annealing temperature [47, 48]. Increasing the mechanical activation time and annealing temperature reduced the crystallite size of akermanite.

4.3 Nanostructure evaluation

Scanning electron microscopy (SEM) was used to characterize the surface morphology of both the base materials as well as akermanite. Fig. 17 shows the SEM
micrographs of the unmilled base materials talc (a,b) calcium carbonate (c) and silica (d). As can be seen, the talc particles were thin sheets that have a width between 10 and 50 µm and have agglomerated. Calcium carbonate particles were shown to be thin rods with a length of 1 µm that have agglomerated together. Silica particles were shown to be highly porous round structures that have diameters between 5 and 30 µm.

The micrographs of akermanite powders synthesized from 10 and 20 h of mechanical activation and subsequently heat treated at 900 °C are shown in Fig. 18. Particles of akermanite were shown to be macroporous structures with a mean size of 50 µm. These larger structures were made up of smaller agglomerated particles. The smaller agglomerated particles were shown to have sizes that range between 50 and 500 nm. Due to the fact that akermanite crystallites had an average size of 35 nm, akermanite particles were therefore made up of numerous nanocrystallites that were agglomerated together. This fact can be seen in the TEM micrographs, shown in Fig. 19, that shows numerous nanocrystallites were agglomerated together. These were therefore forming the smaller particles shown in the SEM results. Additionally, this result agrees with the previous results calculated from the Williamson-Hall method.

It has been shown that the talc system is able to produce nanocrystallite akermanite. The crystallites have a smaller size, of 35 nm, than akermanite synthesized from calcium carbonate, magnesium carbonate, and silica. To further understand this system, a study was performed to determine the effect of mechanical activation on the system. Therefore, TG and MS were performed on mechanically activated powders in order to characterize the system. Additionally, XRD was performed in order to further understand what the effect of mechanical activation has on the system. One of the
weaknesses of the application of akermanite is the low mechanical properties of scaffolds. Hence, akermanite produced from talc was evaluated to determine its mechanical properties.

4.4 Thermogravimetric analysis/mass spectrometry

TG and MS tests were utilized on 20 h mechanically activated powders to characterize the reactions. Fig. 20 a and b depicts the results of TG and MS respectively. The results of TG depicted two major weight loss steps. Additionally, MS analysis showed two major peaks related to the release of CO$_2$. The first peak of CO$_2$ began at 425 °C and finishes by 650 °C. This peak was related to the first weight loss step of 6.5%. The second peak, which was sharper and had a larger magnitude, began at 775 °C and finished by 875 °C. This larger peak was related to the second weight loss step of 6%. Additionally, there was a steady release of H$_2$O, which starts at 25 and lasts until 975 °C. This related to the steady weight loss shown in the TG trace.

Only talc and CaCO$_3$ decomposed, releasing H$_2$O and CO$_2$ respectively. Talc has been shown to release structural H$_2$O during decomposition [28]. There is a theoretical weight loss of 4.7% that can be attributed to this decomposition. However, experimentally it was found to have a different weight loss, of 15% after being heat treated up to 975 °C [28]. The difference between these values can be attributed to the loss of absorbed atmospheric water. Additionally, it is known that CaCO$_3$ releases CO$_2$ during decomposition, with a theoretical weight loss of 44%. Galan et al. [35] determined that crystalline CaCO$_3$, that has a purity above 99%, decomposed with an experimental weight loss of 43%. Additionally, it has been shown experimentally that talc and CaCO$_3$ release
absorbed atmospheric water [29]. This fact could be the reason for the consistent release of H$_2$O, which is seen throughout the TG.

In the TG there was a total weight loss of 19.5%. There was a discrepancy between the theoretical and experimental weight loss of the powder. The theoretical weight loss was higher at 25.6%. This difference between the weight losses could be attributed to the release of volatile materials during mechanical activation. To see if this was true, new powder samples were weighed before and after 20 h mechanical activation. There was a weight loss of 5% after the mechanical activation cycle. Additionally, when opening the ball mill containers, after the cycle was completed, gas was released. This released gas could be the cause of discrepancy between the weight loss values. This is supported by other researchers who made similar observations about differences between experimental and theoretical values [35].

Wieczorek-Ciurowa et al. [30] determined that mechanical activation can have an effect on the location, slope, and number of weight loss steps observed on TG traces. Additionally, mechanical activation has been shown to change the total weight loss. This is further support for the discrepancy between the theoretical and experimental values of weight loss.

4.5 The Effect of Mechanical Activation on X-ray Diffraction

XRD testing was utilized in order to characterize the powders that were mechanically activated and heat-treated. Fig. 21 depicts the XRD traces of the unannealed mechanically activated powders. The following powders: talc, calcium carbonate, and silica, were mixed and mechanically activated at various times. The trace from powders
mechanically activated for 15 min show distinct peaks, which means that the materials were still crystalline in their structure. Peaks related to talc (XRD JCPDS data file No. 00-013-0558) and CaCO$_3$ (Calcite) (XRD JCPDS data file No. 00-005-0586) were visible. However, as shown in Fig. S1, silica was not visible on the XRD traces, due to the amorphous structure of the powder. Further mechanical activation began to shorten and widen the peaks of the base materials. This effect was due to induced stresses, reduced grain sizes, and the powder becoming amorphous in its structure [36]. After mechanical activation of 20 h, the powder became amorphous without any distinct peaks. After heat treating the powder at 500 and 600 °C, there were insignificant changes on the traces, shown in Fig. S5 and S6.

Fig. 22 depicts the traces related to mechanically activated powders that were annealed at 700 °C. The samples that were mechanically activated between 15 min and 3 h showed peaks related to Ca$_3$Mg(SiO$_4$)$_2$ (merwinite) (XRD JCPDS data file No. 00-025-0161) on the XRD traces. Further increasing the mechanical activation time did not produce peaks related to a new phase. Therefore, 700 °C was not sufficient to advance the reactions to develop any new phases. Additionally, talc and CaCO$_3$ did not completely decompose in samples that were heat treated at 700 °C.

Fig. 23 shows XRD traces of powders mechanically activated for various times and annealed at 800 °C. At this temperature, CaCO$_3$ started to decompose into CaO (calcia) (XRD JCPDS data file No. 00-037-1497) and CO$_2$. The decomposition of CaCO$_3$ occurs according to the following reaction [29].

$$CaCO_3 \rightarrow CaO + CO_2$$

(2)

Although CaCO$_3$ has been shown to decompose at 650 °C, it does not completely
decompose [29]. The kinetics of the reaction were too slow at this temperature to fully decompose CaCO$_3$ within 1 h. Additionally, this is in agreement with the results obtained from the TG of mechanically activated powders, shown in Fig. 20, that show the decomposition of CaCO$_3$ occurs in two distinct steps. The XRD peaks related to merwinite began to grow in magnitude due to the growth of the phase.

Fig. 24 depicts the traces of powders that were mechanically activated for various times and annealed at 900 °C. At this temperature the thermodynamics of the system advanced sufficiently so that talc began to decompose into MgSiO$_3$ (enstatite) (XRD JCPDS data file No. 00-003-0520), SiO$_2$, and water even without significant mechanical activation. The decomposition of talc occurs according to the following reaction [45].

$$Mg_3Si_4O_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O$$ (15)

Minor peaks related to enstatite can be seen on the traces of 15 min, 1, and 3 h mechanically activated powders. However, further mechanical activation removes the peaks related to enstatite. This was due to the consumption of this phase in further reactions. Transitionary phases of CaSiO$_3$ (Wollastonite) (XRD JCPDS data file No. 00-010-0489) and Ca$_2$SiO$_4$ (larnite) (XRD JCPDS data file No. 00-002-0866) were also detected.

The synthesis of Ca$_2$MgSi$_2$O$_7$ (akermanite) (XRD JCPDS data file No. 01-077-1149) occurred after powders were heat treated at 900 °C. With at least 3 h mechanical activation, akermanite becomes the dominant phase. Additionally, pure akermanite was achieved after 20 h of mechanical activation. Further increasing the annealing temperature to 1000 °C, shown in Fig. S4, did not show any notable changes in the trace.

Mechanical activation, of the powder, has been shown to have an effect on the XRD traces. Filio et al. [36] showed that mechanical activation can enhance the kinetics of
reactions. Mechanical activation decreases particle size, increased the internal stresses and grain boundaries. These effects have been shown to have a positive effect on the rate of reactions [44]. This fact is due to the nature of diffusion-based reactions. The lower distances of diffusion paths, from the smaller particle sizes, result in quicker reactions as well as a more homogenous final product. This can be observed in the XRD traces of this study. XRD patterns in Fig. 21 depict the visible effect of the decrease of crystallinity and induced stresses caused by mechanical activation. The shortening and widening of the peaks were a result of the decrease in crystallinity and an increase in homogeneity [36, 49]. Changes in reaction rates due to the mechanical activation can be visualized in Fig. 24. Without significant mechanical activation, only minor peaks related to akermanite were able to be obtained within an hour of annealing. Increasing the mechanical activation time to 3 h had the effect of making akermanite become the dominant phase. Further increasing the mechanical activation time to 20 h advanced the kinetics of the system sufficiently so that pure akermanite was able to be synthesized.

Williamson-Hall method was used in conjunction with XRD results to calculate the crystallite sizes of akermanite [25]. It was calculated that crystallite sizes averaged 35 and 34 nm for akermanite synthesized with 10 and 20 h of mechanical activation and subsequent annealing at 900 °C for 1 h.

4.6 Mechanical Evaluation

Table 2 shows the results of the density and porosity tests performed on akermanite tablets. The porosity of the akermanite tablets was shown to be below 1%. This result could be due to the tablets shrinking during the heat-treating cycle. The tablets shrunk
approximately 15% in both their height and diameter. This result may be due to the combination of a high annealing temperature of 1200 °C and a long holding time of 5 h. The temperature was above the recrystallization threshold, which allows for the shrinkage. The density was calculated to be the highest at 2.487 and 2.489 g/cm³ for 10 and 20 h respectively.

Fig. 25. shows the results of the CCS tests performed on the akermanite tablets. These results included the Young's modulus and peak stress of the tablets. Tablets made from akermanite synthesized with 6 and 20 h mechanical activation were shown to have the highest modulus of 3750 and 3800 MPa respectively. Additionally, tablets made from akermanite synthesized with 6 and 20 h mechanical activation were shown to also have the highest peak stress of 24.15 and 24.7 MPa. Furthermore, tablets made from akermanite synthesized with 10 and 50 h mechanical activation were shown to have lower mechanical properties.
Chapter 5: Conclusion

Pure nanocrystallite akermanite (Ca$_2$MgSi$_2$O$_7$) powders were synthesized utilizing the mechanical activation method. Calcium carbonate, magnesium carbonate, and silica powders were milled and heat treated with a single cycle for 1 h to achieve pure akermanite. A crystallite size of 67nm was achieved for 50 h mechanical activation and annealed at 900 °C. For the first time, the formation mechanism of akermanite was studied and reported. This formation mechanism was indirect and occurred utilizing a series of transition compounds including enstatite, wollastonite, larnite, and merwinite. Pure nanocrystallite akermanite powder was also synthesized via mechanical activation and subsequent annealing of talc, calcium carbonate, and silica powders. The formation mechanism of akermanite synthesized from these new materials was also scrutinized. It was determined that this formation mechanism involved the formation and consumption of transition compounds as well as direct formation of akermanite. It was determined that the optimal mechanical activation time and annealing temperatures were 20 h and 900 °C respectively. The crystallite sizes of akermanite were determined to be between 20 and 45 nm. Akermanite tablets with the highest mechanical properties were synthesized from 20 h mechanical activation and heat treated at 1200 °C for 5 h. The tablets had a Young’s modulus of 3800 MPa, an ultimate compressive strength of 24.7 MPa, and a density of 2.489 g/cm$^3$. 
References


15. Gough, J.E., I. Notingher, and L.L. Hench, Osteoblast attachment and mineralized nodule formation on rough and smooth 45S5 bioactive glass


Fig. 1. TG curves of 1 min and 20 h ball-milled powders.
Fig. 2. DSC curves of 1 min and 20 h ball-milled powders.
Fig. 3. XRD traces of samples ball-milled for 1 min with varying annealing temperatures.
Fig. 4. XRD patterns of powder samples ball-milled for 5 h with varying annealing temperatures.
Fig. 5. XRD traces of samples ball-milled for 10 h annealed at various temperatures.
Fig. 6. XRD patterns of obtained powders from ball-milling for 20 h with varying temps.
Fig. 7. XRD patterns of sample powders milled for 50 h with various annealing temperatures.
Fig. 8. SEM micrographs of base materials (a,b) calcium carbonate, (c) magnesium carbonate, and (d) silica.
Fig. 9. SEM micrographs of sample powders ball-milled for 20 h annealed at (a,b) 900 °C and (c,d) 1200 °C.
Fig. 10. STA of 15 min ball milled powder between 20 and 1200 °C.
Fig. 11. STA of 20 hour mechanically activated powder from 20 to 1200 °C.
Fig. 12. X-ray diffraction of powders milled for 15 min and annealed at various temperatures for 1 h.
Fig. 13. XRD traces of sample powders mechanically activated for 3 h with subsequent annealing of various temperatures.
Fig. 14. XRD patterns of starting materials milled for 20 h and annealed at various
temperatures.

Fig. 15. XRD traces of powders mechanically activated for 20 h and annealed at 840 °C for various times.
Fig. 16. Crystallite sizes of akermanite calculated via Williamson-Hall method.
Fig. 17. SEM micrographs depicting the morphology of talc (a,b), calcium carbonate (c), and silica (d).
Fig. 18. SEM micrographs of akermanite synthesized from 10 h (a,b) and 20 h (c,d) mechanical activation and heat treated at 900 °C for 1 h.
Fig. 19. TEM micrograph of akermanite synthesized from 20h mechanical activation, with subsequent annealing at 900 °C for 1 h.
Fig. 20. (a) TG and (b) Mass spectrometry of powders after 20h ball milling time.
Fig. 21. XRD traces of unheat treated powders for various ball milling time.
Fig. 22. XRD patterns of powders heat treated at 700 °C ball milled for various times.
Fig. 23. XRD traces of powders heat treated at 800 °C ball milled for varying times.
Fig. 24. XRD patterns of powders obtained from annealing milled powders at 900 °C.
Fig. 25. Mechanical properties of the tablets from the CCS testing
Fig. S 1 XRD traces of unmilled powdered silica.
Fig. S 2 XRD patterns of base materials milled for 1 h with various annealing temps.
Fig. S 3 XRD patterns of powders milled for 6 h and heat treated at various temps.
Fig. S 4 XRD traces depicting powders ball milled for 10 h with various annealing temps.
Fig. S 5 XRD traces of powders annealed at 500 °C ball milled for various times.
Fig. S 6 XRD traces of powders heat treated at 600 °C with various ball milling times.
Fig. S 7 XRD patterns of powders heat treated at 1000 °C and milled for various times.
### Table 1.

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Table 1. Peak angles and their corresponding (h k l) planes, peak heights, full width at half maximum, and particle sizes for akermanite synthesized from powders milled for 50 h subsequently annealed at 900 °C for 1 h.
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Table 2. Average density and porosity of tablets milled for 6, 10, 20, and 50 h.