

**Synthesis and Characterization of Doped Mayenite as a
Transparent Conducting Oxide**

**A Dissertation Presented
for the
Doctor of Philosophy Degree
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DEDICATION

This work is dedicated to my children, Sarah-Rose Nwamaka Ude (born April 5th, 2013), Krista Mmachukwu Ude, Merrill Chukwuemezie Ude, Chelsea Chinwendum Ude, Jennifer Nneoma Ude, and Daniel Chukwumenakaya Ude. Also, to my mother, Roseline Ijeoma Ugwu, who cherished education but was not given the opportunity to be educated. April 19th, 2013 marks your 25th year of exiting this world, I love you and miss you dearly.

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ABSTRACT

Base and doped mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) were synthesized using both solid-state and citrate gel techniques; and fired in air and reducing atmospheres. The prepared compositions were studied using neutron and x-ray diffraction at room temperature, high temperature x-ray diffraction (HTXRD), differential thermal analysis (DTA), scanning electron microscopy (SEM), digital optical microscopy, and Brunauer, Emmett and Teller (BET) surface area analysis. Electrically conductivity was measured on the Fe (iron) doped samples using a 2-point, after firing in a reducing atmosphere.

The HTXRD data on pure mayenite synthesized using citrate gel method and fired in air showed that the sample remained amorphous until around 750 °C (degrees Celsius) before crystallization started. The first observed phase was CaCO_3 (calcium carbonate), as the temperature increased, other phases including $\text{Ca}_3\text{Al}_2\text{O}_6$ (tricalcium dialuminate), and CaAl_2O_4 (calcium dialuminum) were observed but disappeared with higher temperatures while the mayenite phase increased and was eventually the only phase at 900 °C. The crystallization temperature of CaCO_3 was confirmed by thermal analysis result conducted in compressed air. However, when high temperature x-ray diffraction data were collected in reducing environment, the presence of CaCO_3 was not observed. Scanning electron microscopy results showed that sample prepared using citrate gel technique has more numerous but smaller pores compared to the solid-state prepared sample.

Using the citrate gel method more incorporation of the dopant into the mayenite structure was achieved than using solid-state synthesis. Equilibrium was reached at lower temperatures and shorter time during firing with the citrate acid method compared to the samples prepared using solid-state synthesis. Neutron diffraction data collected on mayenite with 0.3 atomic% Fe confirmed that Fe was replacing Al (aluminum) in the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ framework and an increase in the lattice constant was observed. X-ray diffraction data also confirmed the increase in lattice constant with increasing Fe concentration. Conductivity measurements with a 2-point probe on samples containing Fe and fired in reducing atmosphere showed increased resistivities compared to pure mayenite fired in reducing atmosphere. The different Fe concentrations showed about the same amount of resistance.

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INTRODUCTION

Introduction

Transparent Conducting Oxides

Transparent conducting oxides (TCOs) are characterized by a unique combination of low electrical resistivity and high optical transparency in the visible range of the electromagnetic spectrum. They are an important group of inorganic materials found in nearly every thin film photovoltaic device. TCOs are used in a wide variety of applications in various devices including light-emitting diodes, energy efficient windows, solar cells, flat-panel displays, electro-chromic mirrors and windows, oven windows, touch-panel controls, electromagnetic shielding, invisible security circuits, transparent radio antennas, etc [1].

Factors which may influence the choice of TCO material include chemical and physical durability, thermal stability, work function, deposition temperature, etchability, uniformity, toxicity, and cost [1]. Of great importance is the ratio of electrical conductivity (σ) to the optical absorption coefficient (α) of the transparent conducting material. This ratio is expressed in equation 1-1, and quantitatively measures the performance of these materials. A higher value of this ratio indicates a better performance of the TCO.

$$\sigma/\alpha = -\left\{R_s \ln(T + R)\right\}^{-1} \quad \text{Eq. 1-1}$$

In equation 1-1 R_s is the sheet resistance, T is the total visible transmission, and R is the total visible reflectance [1]. The figures of merit (σ/α) for some of the common TCOs are listed in Table 1 in appendix A.

Transparent conducting oxides usually satisfy two conditions, (1) in order to transmit at least 85% of visible light the band gap should be more than 3.0 eV, and (2) there should be easy transition from semiconductor to metallic conductor [2]. The energy band gaps of different materials are shown in Figure 1 (Appendix A). In order to convert a material of high band gap to a metallic conductor, the oxide should undergo degenerate doping thereby increasing the free carrier density sufficiently to move the Fermi level into the conduction band. Doping to achieve degeneracy requires donors in the form of point defects or impurities with ionization energies close to the conduction band [3]. The product of free-electron concentration and the electron mobility influences the increase in conductivity. The highest concentration of dopant atoms that can be accommodated in the lattice, determines the free-electron concentrations in semiconductors with wide band gaps [1].

Another important factor that affects the properties of TCOs is the preparation/deposition method. Some chemical preparative methods include chemical vapor deposition (CVD), chemical bath deposition, sol-gel, and electroplating; while the physical methods include evaporation, sputter deposition, and pulsed laser deposition [1, 4]. Spray pyrolysis is a type of CVD

and has been commonly used in deposition of TCOs. Other methods include cathodic electro-deposition and anodic conversion [4].

Different TCO candidates are used for different applications and no one candidate might be suitable for all purposes and the method of fabrication might be dependent on application. Some of the common TCOs in use include $\text{SnO}_2\text{:F}$, ZnO , $\text{In}_2\text{O}_3\text{:Sn}$ (ITO) ZnO:F , ZnO:Al , Cd_2SnO_4 , SnO_2 . ITO has been the choice of material commonly used as TCO, dominating the photovoltaic and display technologies. This is because no other TCO material presently has the performance and versatility of ITO. It has been easily deposited by sputtering, CVD, spray pyrolysis, and reactive evaporation; and shows the lowest resistivities of about $1 - 3 \times 10^{-4} \Omega\text{cm}$ [3, 5] and a figure of merit of $3 \Omega^{-1}$ (Table 1). Doped SnO_2 has shown a resistivity of $6 \times 10^{-4} \Omega\text{cm}$ with a figure of merit of $3 \Omega^{-1}$, but the high production temperatures limit its use in certain applications. Doped ZnO has shown improved electrical properties with resistivities of $4 - 5 \times 10^{-4} \Omega\text{cm}$ and figures of merit ranging from 0.2 to $7 \Omega^{-1}$ but still cannot completely replace ITO due to processing and performance issues [1, 3].

Project Motivation

The expanding use of TCO materials, especially for the production of transparent electrodes for optoelectronic device applications, has developed into a huge worldwide economy that depends on the availability of indium for use in ITO.

Indium is a scarce and expensive metal, therefore the cost climbs as the supply is decreasing. In the U.S, 82% of the In consumption is used in the production of ITO, and there are no adequate facilities to recycle enough indium [2]. The high and constant growth in electronic industries coupled with the natural scarcity of indium motivates the search for earth abundant TCOs to replace ITO. Though a large number of alternative binary oxides have been under exploration for some time now, many of which have shown some improvement in properties, none of them has shown sufficient overall properties to completely replace ITO [6]. Also, the realization that properties required of TCOs are dependent on the application under consideration, is driving research into alternative materials and processes for manufacturing TCOs for the specific applications [7].

The demand for less expensive, earth abundant and environmentally friendly TCO materials capable of exhibiting high electrical conductivity and optical transmission is motivating further research. Mayenite type-TCOs are interesting for various reasons; they present a new method of achieving electrical conductivity and optical transmittance, and are based on some of the most earth abundant elements. The band structure analysis of this material suggests the possibility of total transparency as well as high electrical conductivity [8]. The conventional TCO materials cannot be completely transparent because of the inter-band transitions from the partially occupied intra-band. Ti-treated mayenite has been reported to have a conductivity of 1500 S/cm at 300 K [9]. Though this value is small compared to the conductivity found in ITO which is in the range of

8000 - 22000 S/cm [2], ITO has been researched for decades in order to improve this property and with similar efforts on mayenite great improvement in the conductivity can be achieved. Sushko et al. [10] suggested cation substitution, which can reduce the inter-cage distances in the lattice thereby increasing conductivity as well as optical gap.

Background

Mayenite

The compound mayenite is one of the intermediary phases of the $\text{CaO} - \text{Al}_2\text{O}_3$ binary system, stoichiometrically represented as $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. The $\text{CaO} - \text{Al}_2\text{O}_3$ binary phase diagram is shown in Figure 2. Mayenite has been known for decades as a major constituent of calcium aluminate cements with the formula written as $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ or C_{12}A_7 in the 'cement-chemist notation'. The mineral mayenite was originally reported from Eifel volcanic complex in Germany, and found in pyrometamorphic sites [11]. In recent years mayenite has been of interest to researchers given some reported properties as a TCO, a catalyst for the combustion of volatile organic compounds, an ionic conductor, etc.

Crystal Structure of mayenite

Mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) crystallizes in the cubic crystal system with the space group $I-43d$ and has a lattice constant of about 12 Å. The structure is highly porous, with a theoretical density of about 2.63 g/cm³ [11]. The crystal structure

consists of a positively charged framework $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}$ and free oxygen O^{2-} . The framework is made up of a 3-dimensional network of corner sharing $[\text{AlO}_4]$ tetrahedra with seven-coordinated Ca ions resulting in six crystallographic cages of a sub-nanometer size [12]. The result is two types of oxide anions in mayenite: framework oxygens and the cage oxygen (free oxygen) where the latter is randomly distributed within the cages of the framework and serves to maintain the charge neutrality of the entire crystal.

Properties

The material exhibits interesting properties resulting from its unique crystal structure, the structure of mayenite as suggested by Bartl et al. [13] is shown in Figure 3. Stoichiometric mayenite (C_{12}A_7) is a typical insulator having a fundamental band gap of 6-7 eV and gives no peaks in the reflection spectra from 0.3 to 5 eV [14]. The unusual display of electrical properties by mayenite was first reported by Lacerda et al. [15]. As-prepared mayenite exhibit oxide ion conductivity, at high temperature, not far below that of yttria-stabilized zirconia (YSZ). In heat-treating mayenite in a hydrogen environment and subsequently irradiating with ultra violent rays, it was converted into a persistent electronic conductor [16]. Hydride anions are formed at high temperatures in a hydrogen environment, and the formed anions become clathrated in the cage replacing the free oxygen ions. During irradiation with UV light, the clathrated anions are

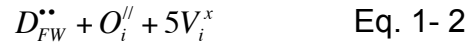
ionized to an OH and electron (e^-) pair. The electron becomes trapped in the cage and behaves like an F -center and hops under an electric field.

Mayenite has also been examined as an inorganic electride [17-19]. Materials that trap electrons at a stoichiometric concentration in solid state are known as electrides. They combine transparency with electronic conductivity, and their electronic properties range from semiconductivity, at low electron concentrations, to superconductivity, at high electron contents. Mayenite, being a nanoporous oxide, has the structure where electrons can replace the oxide anions under ambient condition and still retain thermal stability. This incorporation of electrons into the structure led to the discovery of TCO properties in mayenite [20].

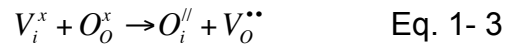
Defects

Point defects can be introduced into mayenite and can be intrinsic or extrinsic. These defects result in ionic and electronic conductivity, and make up the total electrical transport properties. The free oxygen ion in the mayenite structure randomly occupies one of the six chemically equivalent cages, inherently leaving five empty oxygen sites as structural vacancies. There is a distortion of the lattice resulting from the Coulomb attraction between the free O^{2-} ions and two Ca^{2+} ions on the cage wall the oxygen occupies [12, 21]. The empty cages are not equivalent to the occupied cage as depicted in Figure 4. Palacios et al. found the intercage Ca – Ca distance for empty cage in stoichiometric mayenite to be 5.615 Å, and 4.429 Å for the occupied cage [21].

In terms of Kroger-Vink notation, Lee et al [12] suggested that the $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}$ framework might be regarded as a doubly charged pseudo-donor ($D_{FW}^{\bullet\bullet}$) with fixed concentration, and the six cages as neutral interstitial sites (V_i^x). The free cage oxygen may be regarded as doubly ionized interstitial oxygen, $O_i^{\prime\prime}$. The structure may be represented as in equation 1-2:



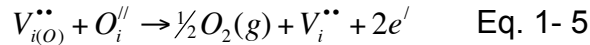
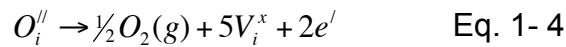
With five unoccupied cages, there is a possibility that a thermal excitation may cause some framework oxygen (O_o^x) to reside at the interstitial sites thereby creating a corresponding number of lattice oxygen vacancies ($V_o^{\bullet\bullet}$) as shown in equation 1-3.



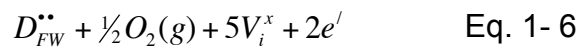
Also, an electron (e') – hole (h^*) pair formation can be established by thermal excitation [12].

Reduction of mayenite

Figure 5a gives an illustration of the electron energy diagram of the insulating stoichiometric $C_{12}A_7$ simplified from theoretical studies [17, 19, 22]. The large free space in the cage, about 0.4 nm in diameter, and the positive charge of the unoccupied cage form a quantum dot-like quantized state. Neighboring cage states couple with the quantized states forming conduction bands called “cage conduction band” (CCB) [21]. From theoretical calculation there is an indication that the CCB is located at 1-2 eV below the bottom of the framework conduction band (FCB) and the 2p levels of the free oxygen ions form the highest occupied state located at ~5 eV below the FCB and ~1 eV above the cage framework valence band (FVB) [23]. When the free oxygen ions are removed from the cages through a reduction process, electrons are introduced to the cages to keep the charge neutrality of the crystal. Equations 1-4 and 1-5 express the reduction reactions.



The reduced mayenite structure can now be represented as shown in equation 1-6:



The electron concentration and electronic states in $C_{12}A_7: e^-$

For low electron concentration, $N_e < 5 \times 10^{20} \text{ cm}^{-3}$, there is a deformation in the cage occupied by an electron resulting from electron-lattice interaction, which is similar to the distortion in the cage occupied by free oxygen ions [17] as shown in Figure 4b. This deformation divides the CCB into empty bands and fully localized bands (F^+ center bands), forming a semiconducting phase as shown in Figure 5b. The electrons exhibit electronic transitions from the localized bands to the empty bands (inter-cage transitions), and a small transition to the excited states in the same cage beneath the FCB (intra-cage transitions) [17]. There is a strong interaction between the encaged electron and the cage framework and the electrons migrate as polarons from occupied cage to the neighboring cage [23].

As the electron concentration (N_e) increases, the deformation of both the electron occupied cage and empty cages becomes smaller [17]. For medium electron concentration, $N_e = 5 \times 10^{20} - 1 \times 10^{21} \text{ cm}^{-3}$, the energy levels in the electron-encaging cages (F^+ center states) and the empty cages becomes closer, and consequently forms hybridized bands of the F^+ center bands and the CCB. The encaged electrons are still localized in the cages but with more electrons in a semi-occupied delocalized band. The electrons undergo inter-cage and intra-cage transitions, showing increased conductivity. The localized and delocalized bands form a continuous density of states in the CCB, with a mobility edge (E_m) that separates the bands [23].

For maximum electron concentration, $N_e = 2 \times 10^{21} \text{ cm}^{-3}$ (when 1/3 of the cages are occupied by electrons), an intra-cage transition is dominant and most of the electrons are delocalized over the cages. The cage deformation becomes very small because of an increased number of encaged electrons, averaging out the cage deformation as the effect of the electron-lattice interaction increases. The averaging of the cage structure makes the energy levels of the occupied cages and the empty cages closer and forms more delocalized CCB, showing metallic conduction [23].

Extrinsic Defect

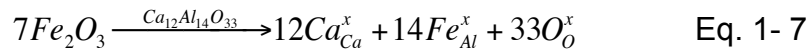
When impurities are introduced in $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ one of the framework elements can be replaced forming a solid solution. Dopants such as Fe, Ti, N, etc, can be added to mayenite and the defect chemical equation can be represented using Kroger-Vink notation as shown in the equations 1-7 through 1-12 below. The defect equations should demonstrate the conservation of mass, charge and lattice ratios in order to obey the laws of a defect equation. Dopant cations are divided into donor centers if their charge is greater than the charge of the framework cation they replace, and acceptor centers if their charge is less. The acceptor introduces extra negative charge(s) while the donor introduces extra positive charge(s) to the lattice [24]. For a stoichiometric solid solution, the charge at the substitution site has to be compensated for by a lattice defect of the opposite charge in order to preserve charge neutrality of the bulk lattice. The extra negative charge of an acceptor can be compensated by either an oxygen

vacancy or a cation interstitial, while a cation vacancy or an oxygen interstitial can compensate the extra donor positive charge. The choice is usually determined by factors such as the ionic radii and the charge on the defect [24]. For instance, when mayenite is doped with Fe^{3+} , it is expected that Fe will go on Al site because the charge of the two are the same and their ionic radii are closer than the ionic radii of Fe and Ca. Likewise, when doped with Ti^{4+} , it is expected that Ti will replace Ca more easily than Al based on their ionic radii. The ionic radii of mayenite framework cations and the possible dopants are summarized in Table 2.

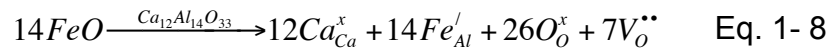
Kroger-Vink notation

Some of the possible substitution reactions when Fe and Ti are individually introduced into mayenite are shown in equations 1-7 through 1-12.

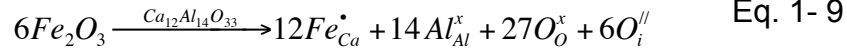
Fe^{3+} in Al position



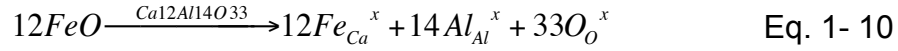
Fe^{2+} in Al position



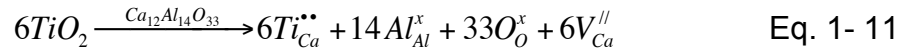
Fe^{3+} in Ca position



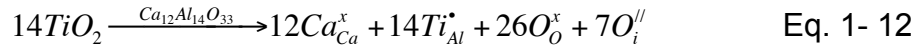
Fe²⁺ in Ca position



Ti⁴⁺ in Ca position



Ti⁴⁺ in Al position

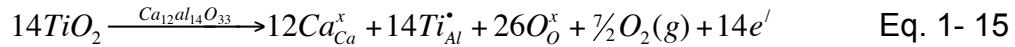


In a reducing atmosphere, there is a shift from stoichiometric solid solution to a non-stoichiometric one, accompanied by a shift from the compensation by a lattice defect to compensation by an electronic defect. For a donor dopant compensated by oxygen interstitials, the excess oxygen is lost leaving behind the charge equivalent of electrons. For the acceptor donor, low oxygen activity creates a lattice deficiency of oxygen, but in an oxidizing atmosphere the vacancies are filled and replaced by the charge equivalent of holes. The replacement of compensating ionic defects by electrons or holes (electronic compensating defects) restores the perfect lattice. These electronic defects can bring about conductivity in a material if they are not strongly trapped by the

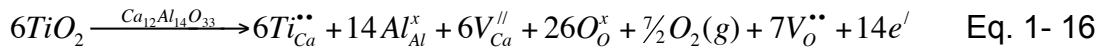
oppositely charged impurity centers. Even when a dopant is compensated by an electronic defect, it is not certain that the electrons or holes will result in high conductivities. The dopant and its compensating defect have opposite charges and there is always the possibility that the electrons or holes will be electrostatically bound to the impurity center [24]. However, the presence of the extrinsic lattice defects helps the reduction/oxidation reactions under conditions where these reactions can consume some of the defects instead of creating them. Therefore, in a reducing environment, the reduction of the interstitial or lattice oxygen proceeds as follow in equation 1-13 and 1-14 respectively, thereby changing some of the above equations as shown in equations 1-15 - 1-17.



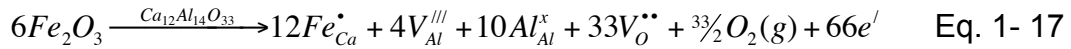
Ti⁴⁺ in Al position becomes



Ti⁴⁺ in Ca position becomes



Fe³⁺ in Ca position becomes



Doped Mayenite

Mayenite has been doped with different cations and anions in order to tailor the electronic structure and hence improve electrical properties. Palacios et al. doped mayenite with gallium using solid-state synthesis and the doped mayenite was characterized using room temperature neutron and x-ray powder diffraction [25]. The doped mayenite (Ca₁₂Al_{14-x}Ga_xO₃₃) showed phase purity up to x = 1 beyond which Ga no longer forms solid solubility with mayenite. The powder diffraction data were analyzed using rietveld method, and the results showed that the lattice parameter increased with Ga incorporation. A joint refinement of the neutron and x-ray powder diffraction data showed Ga was replacing Al in the framework and the substitution occurred more at the Al1 than the Al2 site. The Ga doped mayenite was also treated in a reducing atmosphere and characterized using ultra-high resolution synchrotron x-ray powder diffraction. Analyzed diffraction data indicated that the introduction of electrons into the Ga doped mayenite under reducing atmosphere resulted in decomposition of material.

Bertoni et al. [26] hydrothermally synthesized Si-substituted mayenite (Ca₁₂Al_(14-x)Si_xO_(33+x/2)). Hydrothermal synthesis involves using both low pressure and low

temperature in accessing phases that would not form by ambient condition solid-state synthesis due to their instability at high temperatures. After mayenite was synthesized it was H ion implanted followed by exposure to UV light in order to release electrons. The phase purity of the synthesized mayenite was confirmed using x-ray powder diffraction and the conductivities were measured using the Van Der Pauw technique. The Si doped mayenite showed increased conductivity with increase in substitution level from 0.15 S/cm for $x = 0$ and 0.61 S/cm for the highest level, $x = 4$.

Bertoni et al. also reported on the electronic properties of synthesized Mg doped mayenite ($\text{Ca}_{12-x}\text{Mg}_x\text{Al}_{14}\text{O}_{33}$) prepared by the conventional solid-state techniques [27]. The synthesized mayenite was characterized using x-ray powder diffraction. The diffraction data showed phase purity was obtained up to where $x = 1$ with no significant changes in the lattice parameters. The samples were heat-treated in hydrogen at 1300 °C and subsequently exposed to UV radiation. The conductivity was measured using the Van Der Pauw method, and was found to be dependent on both temperature and Mg content. Increasing Mg concentration resulted in decreased conductivity as Mg was acting as a blocking agent on the conduction path of the hopping polarons involved in conductivity. Mg tends to form clusters, and also strong bonds with the H^- which takes part in the conduction process. Conductivity was reported to increase with temperature but falls off at the hydrogen decomposition temperature (135 °C) as a result of the loss of hydrogen.

Boysen et al. prepared Fe-doped mayenite with 1.0 and 2.5 mol% Fe using the sol-gel method [28]. Neutron powder diffraction and synchrotron x-ray diffraction were used in characterizing the prepared samples. Collected data were analyzed by the Rietveld technique. The result showed that 2.5 mol% Fe-mayenite had CaAl_2O_4 (5.47 wt%) as a secondary phase, and showed an increased in the lattice parameter resulting from Fe having a larger ionic radius than Al which it is replacing in the framework. It was observed that Fe doping of mayenite inhibits the incorporation of extra anions, the nuclear density maps from refinement showed the O position to be diffuse (not well defined) at room temperature and undetectable above 900 °C. The absence of oxygen in the cage was attributed to either a loss resulting from Fe reduction, or extreme delocalization in the cage and hence suggesting that this material could have a high anionic conductivity.

Scope of Work

In this work, the focus is on the crystal chemistry and synthesis of doped mayenite. Chapter I has detailed discussion on using wet chemistry (citrate gel synthesis) to prepare mayenite and comparing the reactions to mayenite synthesized using solid-state techniques; and various characterization techniques including x-ray diffraction, differential thermal/thermo-gravimetric analysis, and viscosity measurements are discussed. The results of high temperature x-ray diffraction and differential thermal analysis were used to study the phase

evolution of mayenite in both oxidizing and reducing atmospheres. Chapter II compares the surface area of mayenite synthesized using both methods and optical and scanning electron microscopy were used to image particles and BET surface area analysis are discussed. Chapter III explores mayenite doped with Fe as a cationic impurity with the intention of creating defects that could enhance conductivity. X-ray and neutron powder diffraction are used to better understand the atomic details of the Fe doped mayenite and the electrical resistance was measured using a 2 point probe and the results here are compared to a previous studies reported in the literature.

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Appendix A

Figures

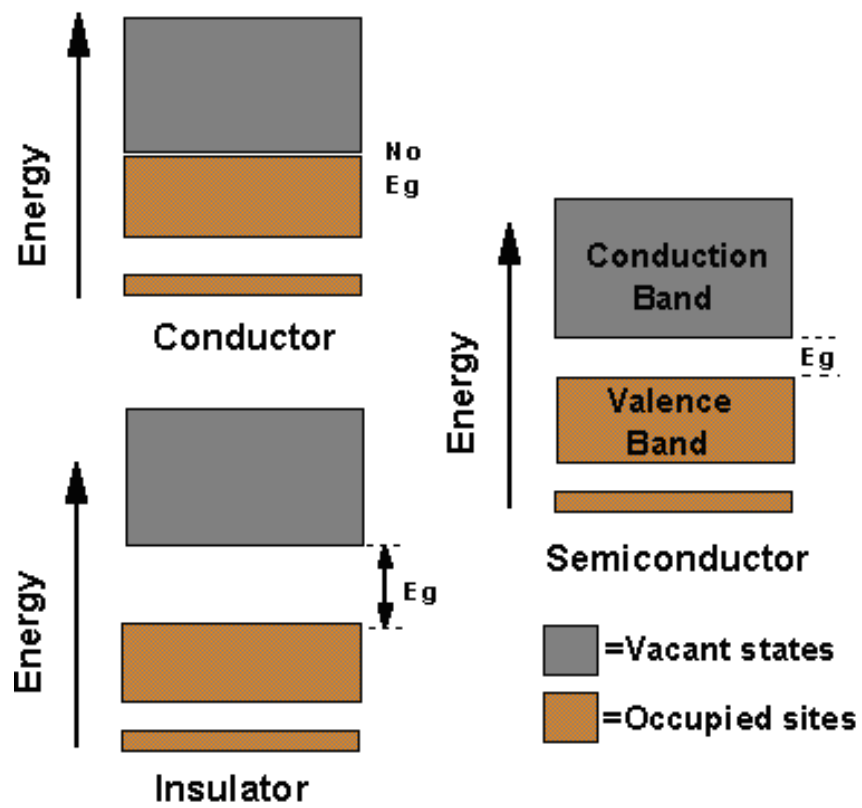


Figure 1. Electronic band structures in solids (B. M. Tissue).

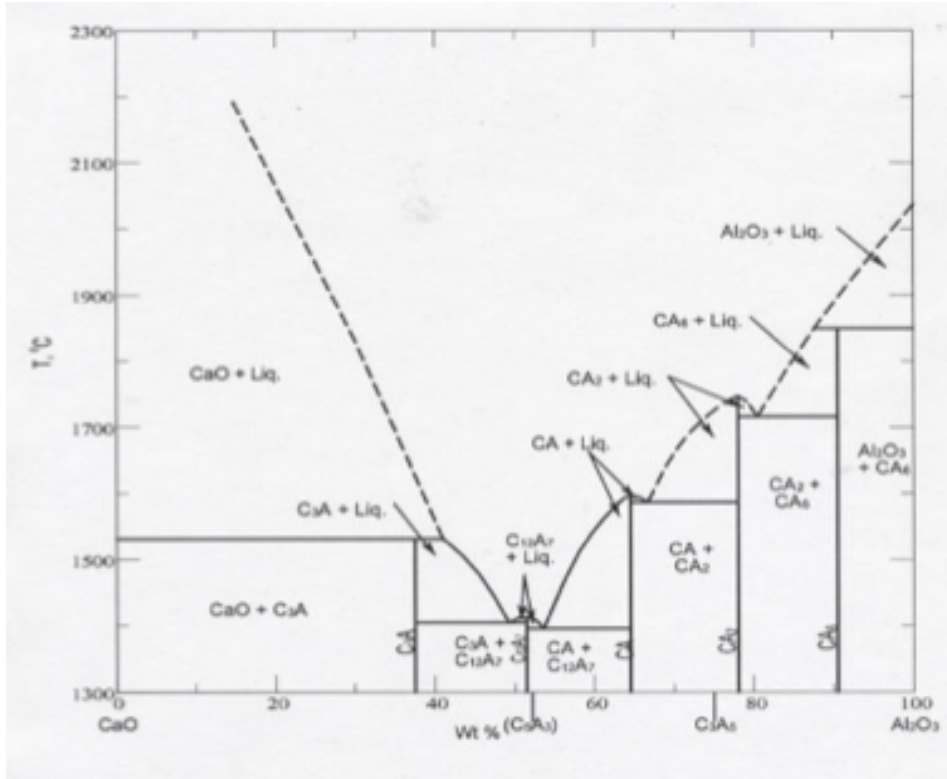


Figure 2. The CaO – Al₂O₃ binary phase diagram (PDFC #231, Vol. 1).

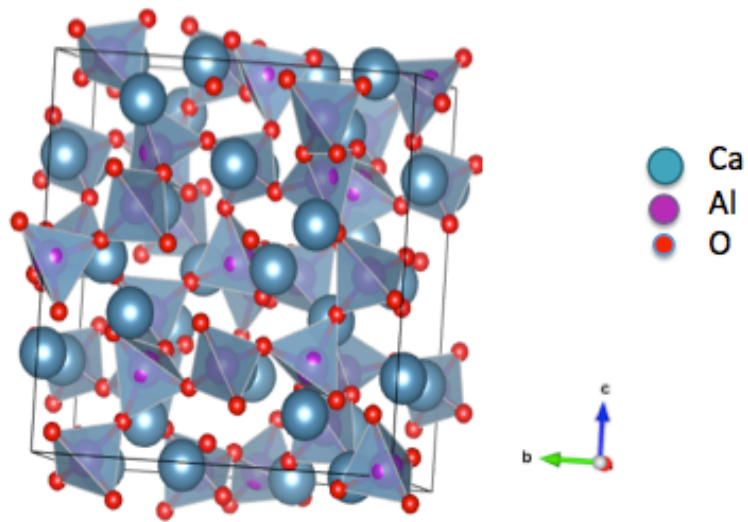


Figure 3. Crystal structure of mayenite drawn from atomic positions reported by Bartl and Scheller [13].

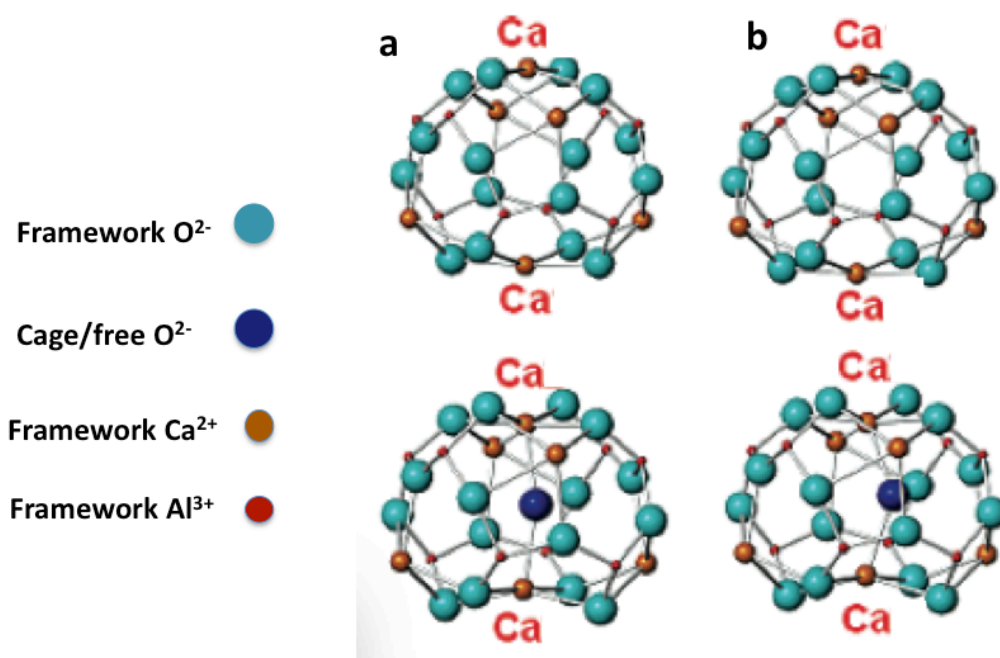


Figure 4. Ball and stick drawing of mayenite cages (a) an empty cage of stoichiometric mayenite (top) and an occupied cage (bottom), (b) an empty cage of non-stoichiometric mayenite (top) and an occupied cage (bottom). (Adapted and modified from Palacios et al. [25]).

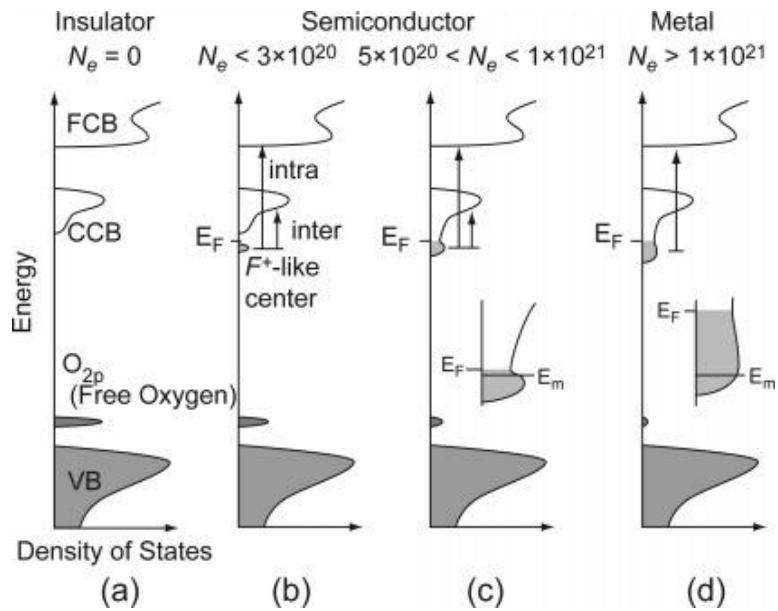


Figure 5. Schematic illustrations of electronic structures of (a) insulating C12A7, (b) low N limit, (c) intermediate, and (d) high N limit C12A7:e. [20].

Tables

Table 1. Figures of merit for some common transparent conducting oxides [1].

Material	Sheet Resistance (Ω/sq)	Absorption Coefficient (α)	Figure of Merit (Ω^{-1})
$\text{In}_2\text{O}_3:\text{Sn}$	6	0.04	4
$\text{SnO}_2:\text{F}$	8	0.04	3
Cd_2SnO_4	7.2	0.02	7
$\text{ZnO}:\text{In}$	20	0.20	0.2
$\text{ZnO}:\text{Ga}$	3	0.12	3
$\text{ZnO}:\text{Al}$	3.8	0.05	5
$\text{ZnO}:\text{F}$	5	0.03	7

Table 2. Ionic radii of mayenite framework cations and dopants [29].

Element	Charge	Coordination Number	Crystal Radius (Å)	Effective Radius (Å)
Al	3+	4	0.53	0.39
		6	0.675	0.535
Ca	2+	6	1.14	1.00
		8	1.26	1.12
Fe	2+	4	0.77 hs	0.63 hs
		6	0.75 ls 0.92 hs	0.61 ls, 0.78 hs
Fe	3+	4	0.63 hs	0.49 hs
		6	0.69 ls, 0.785 hs	0.55 ls, 0.645 hs
Ti	2+	6	1.00	0.86
Ti	3+	6	0.81	0.67
Ti	4+	4	0.56	0.42
		6	0.745	0.605
		8	0.88	0.74
V	5+	6		0.54

*hs – high spin, ls – low spin.

CHAPTER I EXPERIMENTAL

Mayenite was prepared by both conventional solid-state synthesis and a wet chemical method. Different experimental techniques such x-ray and neutron diffraction, scanning electron microscopy, differential thermal analysis, BET surface analysis, were used to characterize the prepared mayenite.

X-Ray Diffraction

X-rays are electromagnetic radiation of short wavelength, generated as a result of periodic acceleration and deceleration of charged particles, especially electrons [1]. When an electron falls through a potential difference of V volts it acquires energy of electron-Volt (eV) expressed as quanta of x-rays of wavelength λ , given by equation 2-1, where e is charge on the electron, h is Planck's constant, c is the speed of light in vacuum [2]. An atomic scattering factor measures the scattering ability of x-ray by an atom and is dependent on the electron distribution and quantity contained in the atom [1].

$$eV = \frac{hc}{\lambda} \quad \text{Eq. 2 - 1}$$

All materials absorb x-rays; absorption increases with the atomic numbers of elements in the absorbing material. The transmitted intensity is expressed according to an exponential law given in equation 2-2, where I_0 is the incident

intensity, x is thickness of the material, and μ is the linear absorption coefficient [3].

$$I = I_0 \exp^{(-\mu x)} \quad \text{Eq. 2 - 2}$$

X-ray diffraction is commonly used in various fields and is used for identifying what phase(s) are present and determining the crystal structure of materials including metals and metal alloys, ceramics, and proteins. The wavelengths of the x-rays are close to the inter-atomic distance in crystals and when an x-ray beam is incident on a crystal that has long-range periodicity in its atomic arrangement, diffraction occurs. The intensity of the diffracted beam is a function of the atoms and their positions in the crystal. When a wave interacts with a single crystal or polycrystalline sample, the incident beam is uniformly scattering in all directions. Figure 6 (appendix B) illustrates the basic principle behind diffraction showing the incident and diffracted waves and the associated angles. The diffraction by a crystal depends on certain phase relations between the interacting waves, which include difference in amplitude and path length. W.L. Bragg established a condition which when satisfied would give rise to diffraction [3]. This is known as Bragg's law and it relates the wavelength (λ) of the radiation to the lattice spacing of the planes of atoms (d) and diffraction angle (θ). The law is expressed in equation 2-3, and n is the order of reflection.

$$n\lambda = 2d \sin \theta \quad \text{Eq. 2 - 3}$$

By changing the angle of the incident waves and the orientation of material and the instrument detector, in a single crystal, it is possible to obtain all diffraction directions in the lattice; these diffraction directions are influenced by the size and shape of the unit cell [4]. Mayenite crystallizes in the cubic crystal system and the equation relating the inter-planar spacing, d_{hkl} , to the cubic unit cell edge, a , for the various reflections, (hkl) and is given in equation 2-4.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{Eq. 2 - 4}$$

The general relationship shown in equation 2-5 is used to predict the diffraction angle for any set of planes and is obtained by combining Bragg's law (equation 2-3) and the plane-spacing equation (equation 2-4) for a cubic crystal.

$$\sin \theta = \frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2} \quad \text{Eq. 2 - 5}$$

Single-crystal diffraction is the best method of determining a crystal structure and allows for detailed information such as the unit cell edges, atomic positions, atomic displacement parameters, and site occupancy factors [5]. However, one limitation of this technique is the requirement of a single crystal. Single crystals are sometimes hard to grow [6] so often powder diffraction, using a polycrystalline sample is commonly used for phase identification determining

lattice parameters, sample crystallinity, phase transitions, thermal expansion, crystallite size, and strain.

For x-ray powder diffraction the material being analyzed needs to be finely ground and homogeneous. The powder becomes equivalent to many crystals randomly oriented, or one crystal rotated about all its possible axes instead of only one axis. Data collection using the powder diffraction method can be fast depending on the detectors and the specific instruments used, and multi-component mixtures can be analyzed with minimal sample preparation.

Diffraction data can be recorded in terms of intensity along the y-axis and 2θ along the x-axis and peak positions are recorded at specific 2θ (degrees) positions. Each phase has a distinctive diffraction pattern based on its crystal structure and the elements that make up the crystal structure. For phase identification both the intensity and peak position are important and a multi-phase sample will have reflections or diffraction maxima for each phase superimposed. The observed data are compared to the diffraction patterns of known materials determined either experimentally or calculated from the crystal structure and stored in databases. One common database is the International Centre for Diffraction Data PDF (powder diffraction file) and in 2011 there was more than 750,000 recorded reference patterns.

The Rietveld method, developed by Hugo Rietveld to analyze neutron powder diffraction data, uses a least squares approach for refining structural parameters and quantitatively determining phase fractions from powder diffraction data. A diffraction pattern is calculated from the crystal structure as well as the instrumental and micro-structural information and the corresponding variables are refined for the calculated pattern to better match the observed data [7]. A good starting structural model is necessary for acquiring structural information and can be obtained from structures reported in the literature including iso-structural materials, theoretical simulations (e.g. Density Functional Theory (DFT)), or high-resolution atomic imaging [8]. In addition to a reasonable starting structural model high quality diffraction data are needed in order to obtain statistically significant results. Adjusting the model parameters (refineable variables) minimizes the differences between the model and each point of the observed pattern. The refined parameters include parameters to model the background, lattice parameters, atomic positions, parameters for modeling the peak shapes including both contributions attributed to the instrument and the sample itself, disorder including atomic substitutions and vacancies on specific atomic sites [8]. Often several rounds of refining are carried out until the patterns match to a great degree without radically revising the model. The measure of the agreement between the two patterns is given as an *R*-factor, which is expressed by various mathematical equations depending on the factor being considered. The *R*-weighted pattern (R_{WP}) is given in equation 2-6, where I_O is observed intensity at i^{th} step, I_C is calculated intensity, w is the weighting assigned at the i^{th}

step. The agreement can also be expressed as goodness of fit (χ^2) shown in equation 2-7, where R_{exp} is the best statistically expected R value [9] and a low value of R_{exp} signifies a high quality data. A low χ^2 signifies a good fit between the observed and calculated pattern, however, a value below one suggests the quality of data cannot be used to determine statistically substantial results.

$$R_{WP} = \left\{ \frac{\sum_i w(I_o - I_c)^2}{\sum_i w(I_o)^2} \right\}^{1/2} \quad \text{Eq. 2 - 6}$$

$$\chi^2 = \left(\frac{R_{WP}}{R_{\text{exp}}} \right)^2 \quad \text{Eq. 2 - 7}$$

Neutron Diffraction

Neutron diffraction is a form of elastic scattering where the incident and diffracted neutrons have approximately the same amount of energy. The principles describing x-ray diffraction above are the same, however, the radiation source is different resulting in different scattering properties [7]. Neutrons are scattered by the nuclei while x-rays are scattered by the electrons in the atoms.

The neutron source can either be a nuclear reactor (constant wavelength) or a spallation source (time-of-flight). Neutrons are transported through neutron guides from the source to the sample and can change their velocity during interaction with the sample. For the time-of-flight diffraction technique, these changes are detected by measuring the time needed for the neutrons to reach the detector after hitting the sample at a given distance. The wavelength of the diffracted beam is related to the velocity, as shown in equation 2-8 where h is the Planck's constant, m is mass of a neutron, and t is the time of flight and L is the path length [6], and is obtained from the measured time and recorded distance.

$$\lambda = \frac{h}{mv} = \left(\frac{h}{m} \right) \left(\frac{t}{L} \right) \quad \text{Eq. 2 - 8}$$

The direction of the scattered neutrons is defined by measuring the scattering angle corresponding to the position of the neutron detector [10]. When neutrons speeds are properly selected, their wavelength usually lies near 1 Å, corresponding to a typical spacing between atoms in a crystalline material with long range order [7]. Since the nuclei are small compared to this wavelength, the intensity of scattered neutrons from a non-vibrating nucleus is not reduced significantly at high angles as compared to x-ray diffraction. This helps in differentiating peaks with lots of intensity at low d or high angles in order to better determine the atomic displacement parameters and/or site occupancy factors in a structure. Also, the scattering factors do not systematically depend on atomic number, Z , of the scattering element [6] and often low Z atoms contribute

strongly to the intensity even in the presence of high Z elements. The neutron beam is scattered according to a specific number of well-defined angles satisfying Bragg's law. The contribution to diffracted intensity in neutron diffraction depends on the isotopes of the element and the scattering lengths vary from isotope to isotope rather than with the atomic number. For instance, hydrogen and deuterium contribute differently to the diffracted intensity; hydrogen has a relatively small in magnitude and negative bound coherent scattering length, b_c ($b_c = -3.7406$ fm) and a large bound incoherent scattering length that contributes to a high background while deuterium has relatively large in magnitude and positive b_c ($b_c = 6.671$ fm) and a bound incoherent scattering length that is about $1/5^{\text{th}}$ that of H [6, 11]. The advantages of neutron powder diffraction include the ability to distinguish isotopes, increased penetration, sensitivity to light atoms and magnetic moments [12]. The crystal structural information obtained from x-ray diffraction data can be complemented by information obtained in a neutron diffraction data. In this work neutron powder diffraction has been used to determine the Fe position in mayenite and the bound coherent scattering lengths of the elements contained in mayenite are given in Table 3 in appendix B.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) provides high-resolution topographical images of a material's surface. It is a non-destructive technique and is widely

used in phase identification. It can measure precisely small objects or features down to 50 nm in size. When equipped with backscattering electron detectors, it is capable of examining crystallographic orientation in materials. SEM is also used to show spatial variations in chemical compositions by obtaining elemental maps or qualitative chemical analyses using Energy Dispersive Spectroscopy (EDS) [13].

Figure 7 shows a schematic of a scanning electron microscope. A typical scanning electron microscope column consists of an electron gun, electron lenses, sample stage, an electron detection system and a set of deflectors, all operating in vacuum. The electron gun is the source of the electrons and accelerates them to energies in the range of 1 to 30 K eV [13]. The energy carried by the accelerated electrons is given off as various signals produced by the interactions between the electrons and the sample when incident electrons are decelerated in a material. The signals consist of backscattered electrons; secondary electrons used in producing images; photons used for continuum x-rays and elemental analysis; diffracted backscattered electrons used in determining orientation and crystal structure; visible light, and heat.

A scanning electron microscope is comparatively easy to operate and data acquisition is fast and minimal sample preparation is required for many applications. However, most instruments require samples to be stable under vacuum. Electron charging may occur during experiment if the sample has poor

electrical conductivity. In order to avoid charging, the specimen is usually coated with a thin conductive film before it is placed in a high vacuum chamber, however, if an experiment is run in low vacuum the need for the conductive coating is not required. EDS detectors cannot detect light elements and many instruments are unable to detect elements with atomic numbers less than 11 [14].

Brunauer, Emmett, and Teller (BET) Surface Analysis

The Brunauer, Emmett, and Teller (*BET*) analysis is a standard method based on adsorption of certain amount of gas (especially nitrogen) at a given pressure to determine surface areas. It allows for comparisons among various materials and was originally developed for multilayer gas adsorption onto flat surfaces. The analysis is usually performed over the range $0.05 < P/P_0 < 0.3$, with the assumption that monolayer formation occurs in this pressure range [15], and P/P_0 is the ratio of the gas pressure to the partial pressure of oxygen. The specific surface area is determined by monolayer formation of gas molecules on the surface, while the presence of pores, pore volume, and pore size distribution may be determined by the capillary condensation principle.

BET analysis is based on several assumptions [16]: (1) adsorption occurs by multilayer formation, (2) the uppermost layer is in equilibrium with vapor phase, (3) the number of adsorbed layers becomes infinite at saturation pressure, (4) a homogeneous surface with no lateral interactions exists among molecules. A

major issue in using accessible surface area in testing BET results from an experimental isotherm is that most materials have defects and defects naturally lower the amount of gas that can be adsorbed and as such affect the reported surface area [15]. Defects can result from the collapse of portions of a crystal, solvent molecules being retained in the sample after synthesis, etc. The BET equation is given in equation 2-9 and can be translated into equation 2-10 shown below.

$$V = \frac{V_M C P}{(P_o - P) \{1 + (C - 1)(P/P_o)\}} \quad \text{Eq. 2 - 9}$$

$$\frac{P}{V(P_o - P)} = \frac{1}{V_M C} + \frac{C - 1}{V_M C} \frac{P}{P_o} \quad \text{Eq. 2 - 10}$$

V is the volume of gas adsorbed per gram of the material, V_m is the monolayer capacity, and C is related to the heat of adsorption [15]. The analysis is performed by plotting $P/V(P_o - P)$ against P/P_o , as shown in Figure 8 [17] producing a graph consisting of low, medium and high-pressure regions. The slope and the intercept of the graph provide information on the two constants V_m and C, and the surface area A can be then calculated using the equation 2-11 below, where σ_o is the cross-sectional area of the adsorbed gas at liquid density, N_A is the Avogadro's number and V_m is the monolayer capacity.

$$A = V_m \sigma_o N_A \quad \text{Eq. 2 - 11}$$

Selecting an appropriate region on the plot is very important, as well as choosing a proper value for the molecular area of the adsorbate [16].

Differential Thermal Analysis

Differential Thermal Analysis (DTA) is a thermo-analytic technique used in observing changes in energy levels of a material as a function of temperature. Changes in temperature are noted in reference to a standard material, which undergoes the same thermal cycles as the material under investigation. The voltage differential developed by the test material during heating is proportional to the changes in energy levels of the material, however, different from the changes in the energy level of the reference material [18]. The features in the graphs are either endothermic or exothermic. An example of a thermo-graph generated for DTA is shown in Figure 9.

The thermo-graph is characteristic of the sample and with reference to the standard material can be used for material identification. However, the DTA curve is most useful in determining thermal information such as melting temperature, vaporization point, phase transition and crystallization temperatures, and/or temperatures of reaction [18]. The area under a DTA peak

gives the enthalpy change of the sample, which is not affected by its heat capacity [19].

In order to detect small changes in energy using DTA, the instrument used should be able to detect and convey minute information in energy level changes of the sample. It should also have good resolution in order to differentiate between complex reactions [18]. Recent technology has incorporated Thermo-Gravimetric Analysis (TGA) into DTA, and the instrument is able to give both thermal and mass loss information at the same time. Some instruments are also able to provide information on temperature, mass loss, as well as heat flow of a sample simultaneously [19].

Conductivity Measurements

Understanding some of the electrical properties of a material involves measuring the directional motion of electrons under an applied force. Electrical conductivity (σ) is the reciprocal of electrical resistivity (ρ) and measures how well a material tolerates this movement of electrons, while electrical resistivity measures the material's resistance to the flow of an electric charge. Conductivity is expressed in Siemens per meter (S/m) while resistivity is measured in ohm-meter (Ωm). Conductivity and resistivity are affected by a materials chemical composition, crystalline structure, and defects.

Due to the temperature dependence of electrical properties they are commonly measured at 20 °C [20]. While conductivity of most materials decreases with temperature, their resistivity increases with temperature due to an increase in the lattice defects, which also increase with temperature and hinder the movement of charges [20].

Resistivity depends on the densities of free electrons (n) and holes (p) as well as their mobilities (μ_n and μ_p), as represented in equation 2-12 [21].

$$\rho = \frac{1}{q(n\mu_n + p\mu_p)} \quad \text{Eq. 2 - 12}$$

Resistivity can be measured at a probe station using a 2-point probe, 4-point probe, or Van Der Pauw's method, which is a type of 4-point arrangement but measures a sample of arbitrary shape. The 2-point and 4-point arrangements are shown in Figure 10.

The 4-point probe is commonly used in measuring the resistivity of semiconductors; though the data interpretation is easier when using a 2-point probe but 4-point probe tends to eliminate the contact and probe resistance so the actual resistance of the material under test can be better measured. [21]. The total resistance (R_T) measured, shown in equation 2-13, is the sum of the probe

resistance (R_P), the contact resistance (R_C) and the resistance (R_{DUT}) of the material under test.

$$R_T = \frac{V}{I} = 2R_C + 2R_P + R_{DUT} \quad \text{Eq. 2 - 13}$$

Current is passed through the two outer probes and the induced voltage is measured in the two inner probes. The resulting resistance is given in equation 2-14 where s is the equal spacing between the probes, V is the voltage, and I is the applied current.

$$\rho = 2\pi s \frac{V}{I} \quad \text{Eq. 2 - 14}$$

There is a correction factor F which corrects for the sample thickness, diameter, temperature, and probe placement. Adding the correction factor equation 2-14 becomes equation 2-15:

$$\rho = 2\pi s F \frac{V}{I} \quad \text{Eq. 2 - 15}$$

For bulk resistivity, with a sample thickness t , the resistivity is given as shown in equation 2-16.

$$\rho = \left[\frac{\pi t}{\ln(2)} \right] \frac{V}{I} \quad \text{Eq. 2 - 16}$$

While for very thin samples the sheet resistivity is given as presented in equation 2-17 [21].

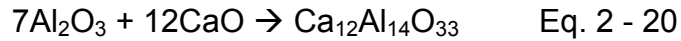
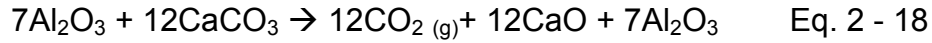
$$\rho = \left[\frac{\pi}{\ln(2)} \right] \frac{V}{I} \quad \text{Eq. 2 - 17}$$

Synthesis and Characterization

Solid-state synthesis

Solid-state synthesis is commonly used in preparations of ceramic powders. The synthesis involves direct combination of two or more powdered materials at high temperature. The technique often requires an initial lower temperature firing or calcination step where CO₂ or other volatiles are driven off. Subsequent higher temperature firings involve chemical reactions between the raw materials to form new phase/s. This synthesis technique is common in the production of complex oxides such as ferrites, titanates, and silicates [22]. Mayenite has been prepared extensively using the solid-state synthesis and most of the reported physical properties of mayenite have been obtained on samples synthesized using this technique.

In this study, mayenite was prepared using solid-state synthesis by reacting aluminum oxide and calcium carbonate or aluminum oxide and calcium hydroxide. During calcination the carbonate decomposed into calcium oxide and CO₂ while the hydroxide broke down to calcium oxide and H₂O. At higher temperatures, the CaO then reacted with Al₂O₃ to form mayenite. The reactions are as shown in equations 2-18 – 2-20.



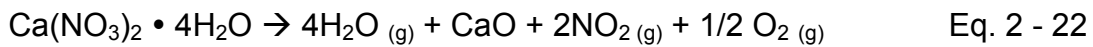
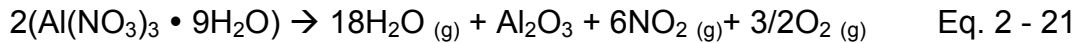
For undoped mayenite samples the powders of CaCO₃ and γ -Al₂O₃ were appropriately weighed and thoroughly mixed with methanol using an agate mortar and pestle. After drying the powder was pressed into a pellet using a 13 mm die. The pellet was fired in an alumina crucible at 1200 °C for 16 hours, and then reground in the agate mortar and pestle, re-pressed, and fired at 1350 °C for 23.5 hours then air quenched. For the Fe doped mayenite samples varying contents of Fe₂O₃ (either Ca_{12-x}Fe_xAl₁₄O₃₃ or Ca₁₂Al_{14-x}Fe_xO₃₃) were weighed out and added to CaCO₃ and γ -Al₂O₃ and the above steps were repeated. The first firing was at 1000 °C for 16 hours and the final firing at 1200 - 1350 °C.

Sol-gel synthesis

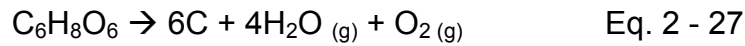
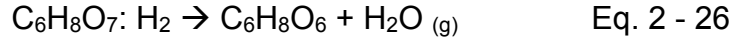
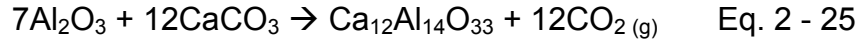
Sol-gel synthesis involves the conversion of a solution of molecular precursors by a chemical reaction into a sol or gel upon drying that is followed by a high temperature firing where the formed sol/gel is transformed into a crystalline material [23]. The process is cost-effective and involves no difficult technical challenges arising from using special equipment. Initial syntheses are often conducted under ambient conditions and usually do not require any need for creating special environments. The precursors are mixed in solution allowing them to interact more easily and form a homogeneous mix [24]. It is a technique widely used in thin film deposition because it ensures the formation of uniform thin films. Samples produced by sol-gel normally do not need as high of firing temperatures as those synthesized using conventional solid-state synthesis. This makes the gel technique useful when making samples that are unstable at high temperatures. Citrate gel synthesis is a type of sol-gel technique where citric acid is used along with other reactants. The citric acid is a type of weak alpha-hydroxy-carboxylic acids that have the ability to form polybasic acid chelates with various cations [25] and ensures the cations are uniformly distributed in the mixture.

In preparing mayenite using the citrate gel synthesis metal nitrate hydrates were dissolved in de-ionized H₂O and citric acid as the organic fuel was added to aid the reaction. The amount of citric acid is based on mole-to-mole ratio of the total number of cations in the nitrates. A series of reactions take place before the final

product is achieved. The nitrates are broken down to their respective oxides at temperatures between 400 – 600 °C. Additional by-products may be formed and broken down along the way. Although the nitrates are dissolved in de-ionized water and well mixed at low temperature, the mixture does not affect the individual decompositions of the nitrates. The nitrate hydrates' decomposition reactions and that of the citric acid are shown in equations 2-21 – 2-23 below.



The citric acid decomposes into CO_2 and H_2O above 175°C [26]. When firing in air the CO_2 reacts with the CaO from calcium nitrate to form CaCO_3 (equation 2-24) at approximately 750°C. The CaCO_3 subsequently decomposes at about 825°C giving off CO_2 [27], while the remaining oxide reacts with aluminum oxide to form mayenite as shown in equation 2-25. However, when firing in a reducing atmosphere CaCO_3 is not formed, the citric acid becomes hydrogenated and at about 192°C decomposes into $\text{C}_6\text{H}_8\text{O}_6$ and H_2O as presented in equation 2-26. $\text{C}_6\text{H}_8\text{O}_6$ subsequently decomposes leaving behind a trace of carbon (equation 2-27), which does not take part in the final reaction to form mayenite.



To achieve the above results, appropriate amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were measured and the nitrates were dissolved in de-ionized water. For doped samples the nitrates of the dopants were also dissolved along with these two nitrates. The solution was heated in an oil bath on a hot plate up to 60 °C before adding the citric acid. The citrate-nitrate mixture was heated to approximately 80 - 90 °C and vigorously stirred with magnetic stir bar until a gel formed (about 4 - 7 hours). The time to gel formation depends on the quantity of water used and temperature applied during the heating. Once a gel results it was placed in a drying oven over night at slightly above 100 °C to dry off the H_2O and is transformed into a cake-like structure, which was subsequently crushed into powder using an agate mortar and pestle. The powder was then divided and some of the powder was used to press pellets for subsequent firing while the remainder was used for subsequent firing in powder form. The firing temperatures varied depending on the subsequent

characterization steps, however, the firing duration was between 3 - 4 h. For the samples fired in reducing atmospheres, either 4% H₂/96% N₂ or 4% H₂/96% Ar, the firing was at 1200 °C under the flowing gas for 6 hours.

Gel viscosity measurement

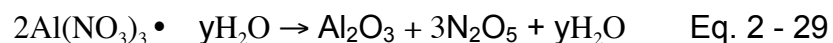
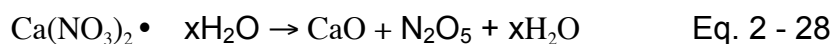
The viscosity of the gel formed using the citrate gel synthesis was measured at room temperature using the parallel plate rheometer RDS-1. The plate has a surface diameter of 25 mm and the thickness of the gel on the plate was 0.821 mm, while a stress of 300 Pa was applied during the measurement. The zero shear viscosity was measured using the dynamic sweep.

Characterization of the Nitrates

The starting reagents for citrate gel synthesis of mayenite are calcium nitrate hydrate, Ca(NO₃)₂ • 4H₂O and aluminum nitrate hydrate, Al(NO₃)₃ • 9H₂O. Both compounds are hygroscopic and due to their absorption of extra moisture the initial amounts weighed out can be slightly lower than required resulting in compositions near but not on the line compound stoichiometry. Therefore, the cations were analyzed in order to know the exact amount of each contained in their corresponding nitrate hydrate.

The nitrate hydrates were separately dissolved in warm de-ionized water to make saturated solutions; 10ml of each solution was gradually heated on the hot plate

until the water evaporated and a powder remained. The powder was further dried in a drying oven where the temperature was slightly above 100 °C and was then subsequently fired at 1000 °C for four hours where decomposition occurred. The resulting compounds from the firing were the metal oxide of each compound (CaO and Al₂O₃), getting rid of the water and N₂O₅. The decomposition reactions are shown in equations 2-28 and 2-29. The oxides were quickly weighed after firing, especially quicklime since it absorbs moisture fast. X-ray diffraction was used to confirm the phase purity of the resulting oxides.



In-situ High Temperature XRD

High temperature XRD was used to study mayenite synthesized using the citrate gel method. Data were collected using a PANalytical X'Pert PRO MPD - diffractometer equipped with an Anton – Paar XRK 900 environmental chamber with a deep well sample holder with a maximum operating temperature of 900 °C in air. Data were collected using Cu K α radiation at 45 KV and 40 mA. The powder was heated from 100 °C to 875 °C at 5 °C per minute and isothermal data were collected every 25 °C. Data were collected over 2 θ range of 15 – 65 degrees and each data collection lasted approximately 10 min. When starting

with powder that had only previously been dried at slightly above 100 °C a drastic volume reduction (2/3's or greater) of the powder occurred at higher temperatures as the volatiles were removed. To leave an adequate amount of powder for high quality data collection subsequent powders for HTXRD experiments were calcined at either 450 °C or 650 °C for one hour and then data were collected every 10 min on the pre-calcined powder at either 850 °C or 875 °C.

For experiments at higher temperatures, the PANalytical X'Pert PRO MPD - diffractometer with Anton Paar HTK16 environmental chamber was used; the heater Pt strip as a sample stage and can be heated up to 1600 °C in vacuum, air, or inert environments. The instrument was operated at 45 KV and 40 mA using Cu K α radiation. Data were collected in air at 800, 850, 900, 950, 1000, 1050 and 1100 °C with a new sample for each temperature. Scanning an entire 2θ range (15 – 65°) took about 20 min allowing for 12 scans over 4 h to be collected at isothermal conditions. Data were collected at the same temperatures and additionally at 1100 °C and with the same time schedule in a 4% H₂/96% N₂ environment.

Complications with water-cooled Pt heater strips arise due to thermal gradients. These thermal gradients exist (1) along the length of the strip due to the water-cooling at the ends, and (2) along the thickness of the sample. The interfacial

thermal contact resistance also contributes to the surface of the sample being at a lower temperature than the heat strip itself [28]. As a result, the two thermocouples in the chamber have different readings at any given time; one thermocouple controls the set point, while the other thermocouple reads a reference temperature. In order to verify the accurate temperature readings on the instrument a temperature calibration was performed using Al_2O_3 and MgO standard reference materials, both with well-established coefficients of thermal expansion, as well as the K_2SO_4 standard reference material with known phase transitional temperatures.

X-ray diffraction data were collected at different temperatures on each of the three samples. By refining the lattice parameters and using the known volumetric coefficients of thermal expansion of MgO and Al_2O_3 , the actual temperatures of the samples were determined. When refining the lattice parameters the sample surface displacement was also refined since this variable is highly correlated with the lattice parameter. Additionally, micro-optical pyrometer (Pyrometer Instrument Company Inc), optical pyrometer using the 'disappearing filament method' was used to determine the temperature of the mayenite powder during the study. Three observers confirmed the color of the filament matching the color of the powder during the experiment.

DTA (Differential Temperature Analysis) was performed in order to confirm the temperatures and transitions observed during the experiments. Data were

collected in an Ar environment from room temperature to 1100 °C, with a heating rate of 5 °C/ min. The powder remaining after the DTA experiment was x-rayed and then re-fired in air at 1100 °C for 4 h.

Study varying the amount of citric acid

Samples were synthesized with lower amounts of the normally weighted citric acid to determine if variations would result from different amounts of citric acid during synthesis. Instead of a mole-to-mole ratio, $\frac{1}{2}$ mole of citric acid to one mole of total cations was used. The obtained powder was pre-calcined at 450 °C for one hour. Time dependent in-situ x-ray diffraction were collected at 800, 850, 900, 950, 1000, 1050, and 1100 °C where each scan took 20 min and three scans at each temperature were collected. Additional in-situ XRD data were collected at 900 °C using 20 min scans collecting data for approximately 6 h.

Results

Gel Viscosity

Figure 11 is a log-log plot of the zero shear viscosity (η) versus frequency (ω). The zero shear viscosity was found to be 94.46 Pa/s, and the plot shows that viscosity was fairly constant until it reaches a frequency of about 1.5 and then increases rapidly with further increase in frequency.

Nitrates characterization

The molar concentrations of the oxides from the decomposed nitrates were calculated using the known volume, molecular mass and measured weight using equation 2-30 below. Furthermore, the amounts of the metal cations were calculated from the measured weights of the oxides.

$$Conc. = \frac{Mass}{Vol. \times MolarMass} \quad \text{Eq. 2 - 30}$$

In a 10ml solution of calcium nitrate, the weighted mass of the CaO was measured to be 0.87 g and the calculated concentration was 1.55 M. The amount of Ca was found to be 0.62 g with a concentration of 1.55 M. While the mass of Al₂O₃ was 0.51 g and the concentration was 0.50 M, and Al was calculated to be 0.27 g with a concentration of 0.50 M.

In-situ HTXRD

Figure 12 shows the room temperature x-ray powder diffraction pattern collected on unfired citrate gel powder showing no crystalline phase in the unfired state. After pre-calcination of the powder at 650 °C for an hour, the diffraction pattern, shown in Figure 13, has a lower background but still indicates the sample is still amorphous. Figure 14 compares the x-ray diffraction data collected as the temperature is increased from 100 to 875 °C over time and shows the background gradually decreasing with increasing temperature and the

amorphous sample becoming crystalline CaCO_3 . This transition from amorphous to crystalline phase was confirmed by DTA to be around $750\text{ }^\circ\text{C}$, this is discussed more in chapter II. Figure 15 shows the x-ray diffraction data collected on the pre-calcined powder at $850\text{ }^\circ\text{C}$ over time, with the most intense peak occurring from CaCO_3 and decreasing in intensity over time. CaCO_3 is reported to decompose between $825 - 850\text{ }^\circ\text{C}$, the predominant CaCO_3 phase observed here confirms the temperature readings on the surface of the sample are lower than the set point of the heating stage. When the powder was fired at $875\text{ }^\circ\text{C}$ over time, the diffraction data (Figure 16) show multiple crystalline phases in addition to CaCO_3 which disappeared over time leaving $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_3\text{Al}_2\text{O}_6$.

Temperature Calibration

As expected the temperatures of the sample surfaces were lower than the set points. The difference between the two temperatures was larger at higher temperatures, up to about $220\text{ }^\circ\text{C}$ around $1000\text{ }^\circ\text{C}$ for Al_2O_3 and $120\text{ }^\circ\text{C}$ around $1200\text{ }^\circ\text{C}$ for MgO . Figure 17 shows the graphs showing the differences between the set points and the actual temperatures, for the MgO standard, as determined from the refined lattice parameters and the known volumetric coefficient of thermal expansion of MgO [29]. Table 3 and Table 5 show the set temperatures and the calculated temperatures for Al_2O_3 and MgO respectively, while Table 6 lists the set points compared to the identified phases at each temperature for the K_2SO_4 . The K_2SO_4 phase transition temperature from orthorhombic to hexagonal

is at 583 °C [30], but the set temperature reading was 700 °C confirming that the actual temperature is lower than the set point reading on the instrument. Table 7 summarizes the temperatures determined by the optical pyrometer during the experiment. The temperatures determined using the optical pyrometer occurred between the set points and the reference points (readings from the thermocouple positioned above the sample).

Table 8 summarizes the identified phases refined from the XRD data collected on the citrate gel synthesized mayenite powder, at various temperatures, based on the pyrometer readings, and durations. The first scan taken at 810 °C showed the presence of CaCO_3 and CaAl_2O_4 , and after 2 hours other peaks belonging to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, and $\text{Ca}_3\text{Al}_2\text{O}_6$ were present. After firing and cooling to room temperature, the diffraction data collected showed $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (63.9 wt%), $\text{Ca}_3\text{Al}_2\text{O}_6$ (10.8 wt%), and CaAl_2O_4 (25.3 wt%). The first data collected at 825 °C shows CaCO_3 , however, the data collected after sitting at 825 °C for 2 h and the subsequent room temperature data do not show CaCO_3 as well as data collected at higher temperatures, supporting the decomposition of calcite around 825 °C. The room temperature data collected after the 850 and 905 °C in-situ experiments show the only phase present was mayenite, however, the room temperature data collected after the 940 °C in-situ experiment shows both $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (89%) and $\text{Ca}_5\text{Al}_6\text{O}_9$ (11%) were present. The first data collected at 1055 °C shows only mayenite phase but the room temperature data collected after sitting at 1055 °C for 2 h shows $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, $\text{Ca}_5\text{Al}_6\text{O}_9$, and Pt_3O_4 . The

presence of Pt_3O_4 is most likely from the Pt heater strip oxidizing or from a reaction between the Pt strip heater and mayenite occurring at higher temperatures.

The diffraction data collected in the 4% H_2 /96% N_2 atmosphere at 800 °C showed only an amorphous phase after firing for 1 h. However, data collected at 850 °C after 10 minutes showed single-phase mayenite. Data collected after firing for 1 h at 850 °C and higher temperatures showed mayenite, $\text{Ca}_3\text{Al}_2\text{O}_6$, and $\text{Ca}_5\text{Al}_6\text{O}_9$ present. Table 9 is a summary of the phases present at different temperatures and times. After firing in the 4% H_2 /96% N_2 atmosphere the resulting powder was black compared to the starting white powder and the white powders obtained after firing in air.

After the DTA/TGA experiment performed in an oxygen deficient environment the resulting powder was also black. Figure 18 shows the TGA results of weight % and derived weight % versus temperature. More details on the results of this analysis are given in Chapter II. The x-ray powder diffraction pattern obtained on the DTA sample after the thermal analysis showed both $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_5\text{Al}_6\text{O}_9$, with the major phase being $\text{Ca}_5\text{Al}_6\text{O}_9$ (92.7 wt%). This result is expected due to the oxygen free atmosphere where the DTA experiment was run. $\text{Ca}_5\text{Al}_6\text{O}_{14}$ is a meta-stable phase of mayenite whose formation is favored in oxygen deficient environment and also at higher temperatures [31]. A major distinguishing factor between the two phases is the Ca–Ca coordination number,

the Ca in $\text{Ca}_5\text{Al}_6\text{O}_{14}$ is octahedrally coordinated and the polyhedral are edge sharing compared to edge and face sharing tetrahedrally coordinated Ca as found in mayenite [32]. Figure 19 compares the Ca polyhedra of the two compounds [31]. The structures and properties of the two compounds are compared in Table 10. After re-firing in air the black powder returned to white and x-ray powder diffraction data collected on the sample showed approximately equal amounts of both $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_5\text{Al}_6\text{O}_9$. The identified phases obtained from x-ray diffraction data on samples fired in different atmospheres are summarized in Table 11.

Quantity variation of citric acid

Figure 20 shows the x-ray powder diffraction data collected on the sample prepared with the reduced amount of citric acid and fired ex-situ in air at 1100 °C for 3 hours. The diffraction pattern shows the presence of both $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_5\text{Al}_6\text{O}_9$, with a higher percentage of $\text{Ca}_5\text{Al}_6\text{O}_9$ (89.8%) compared to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (10.2%). This is most likely due to the reduced amount of oxygen in the $\frac{1}{2}$ citric acid compared to the full citric acid sample. Table 12 and Table 13 show the phases identified using in-situ XRD at various temperatures for both the samples prepared with full and $\frac{1}{2}$ of the citric acid, respectively. At 1100 °C the $\frac{1}{2}$ citric acid sample has both $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_5\text{Al}_6\text{O}_9$ compared to the full citric acid sample which shows phase pure $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

In-situ x-ray diffraction data collected at 900 °C over time on the sample with ½ mole% citric acid is shown in Figure 21. The data has an unequilibrium assemblage of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, $\text{Ca}_3\text{Al}_2\text{O}_6$, and CaAl_2O_4 after 10 min, while the data collected after 40 min showed single-phase mayenite and the phase purity was maintained until the end of the experiment. Figure 22 shows diffraction data collected at 900 °C after 40 min confirming phase purity.

Thermal Expansion

The coefficient of thermal expansion of mayenite was calculated using the lattice parameters refined from the diffraction data collected on the ½ citric acid sample at temperatures in the range of 900 - 1100 °C with 50 °C interval between temperatures. As expected the lattice parameters increased with temperature and Table 14 gives the refined lattice parameters at each temperature. The coefficient of thermal expansion, α , was calculated and using equation 2-31 below, where a is the lattice constant at temperature T . The obtained result was $6.24145 \times 10^{-6} \text{ K}^{-1}$ at 1100 °C and is closely related to the literature value, $6.36 \times 10^{-6} \text{ K}^{-1}$ at 700 °C [33].

$$\alpha = \frac{\Delta a}{a_0 \Delta T} \quad \text{Eq. 2 - 31}$$

Summary

In order to better understand the amounts of cations/oxides present in starting at the beginning of the experiment the starting metal nitrate hydrates have been characterized. Measured viscosity on a gel prepared using the citrate gel synthesis was found to increase with increasing frequency. Prior to data collection on mayenite samples temperature calibrations were performed using standard reference materials and an optical pyrometer on the Pt strip heater on which data would subsequently be collected. As expected the set points were higher than the actual temperatures of the sample surface. High temperature x-ray diffraction data collected in air showed that the phase evolution of mayenite starts with crystallization of calcite at about 750 °C from an amorphous sample and as temperature increases other phases such as $\text{Ca}_3\text{Al}_2\text{O}_6$, $\text{Ca}_5\text{Al}_6\text{O}_9$, CaAl_2O_4 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ are observed until the reaction reaches equilibrium, and ends with single phase mayenite at around 850 - 900 °C. In a reducing atmosphere, mayenite is first to be detected, however, at higher temperatures the meta-stable phase $\text{Ca}_5\text{Al}_6\text{O}_9$ is produced. $\text{Ca}_5\text{Al}_6\text{O}_9$ is also observed when a lower amount of citric acid is used during the synthesis. $\text{Ca}_5\text{Al}_6\text{O}_9$ is favored at higher temperatures and with less oxygen.

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Appendix B

Figures

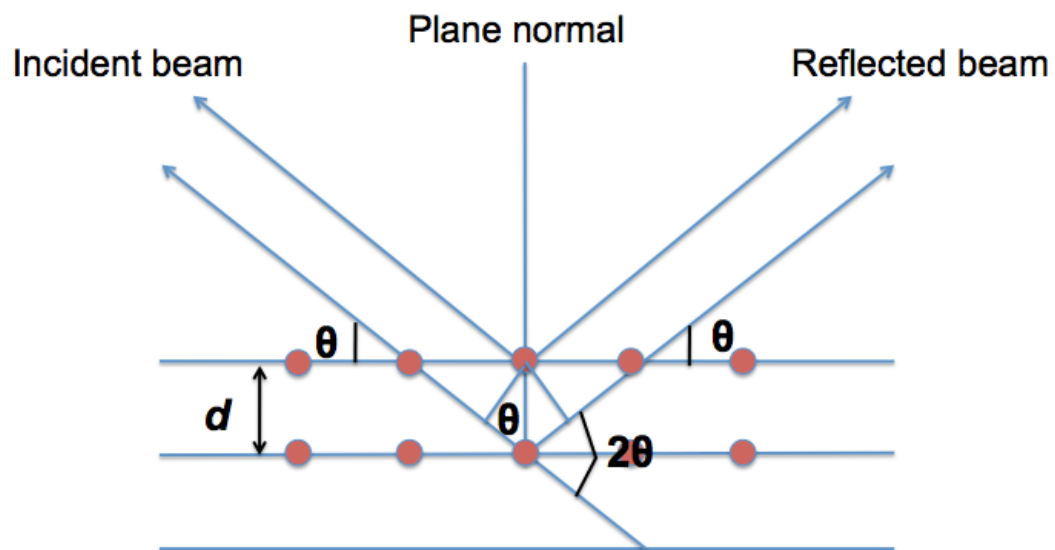


Figure 6. Schematic diagram of x-ray diffraction by atomic planes. (Adapted and modified from Cullity, [3]).

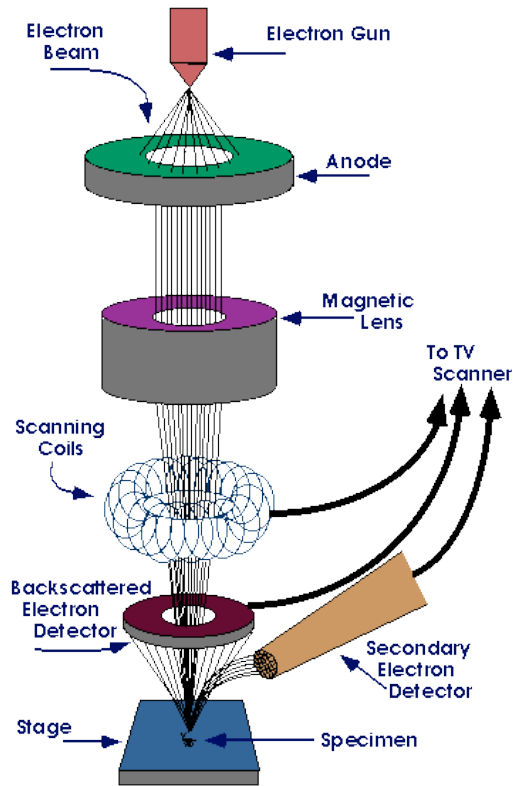


Figure 7. Schematic of scanning electron microscope column [34].

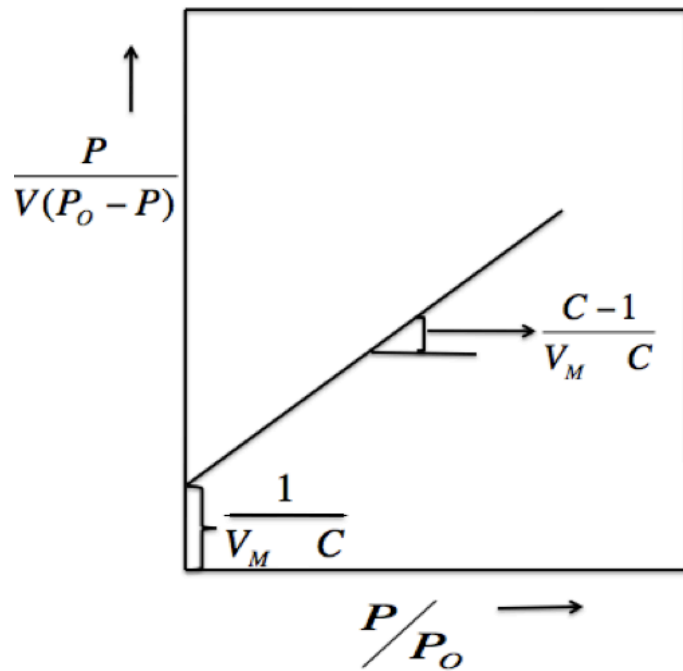


Figure 8. Schematic BET response used in calculating surface area [4].

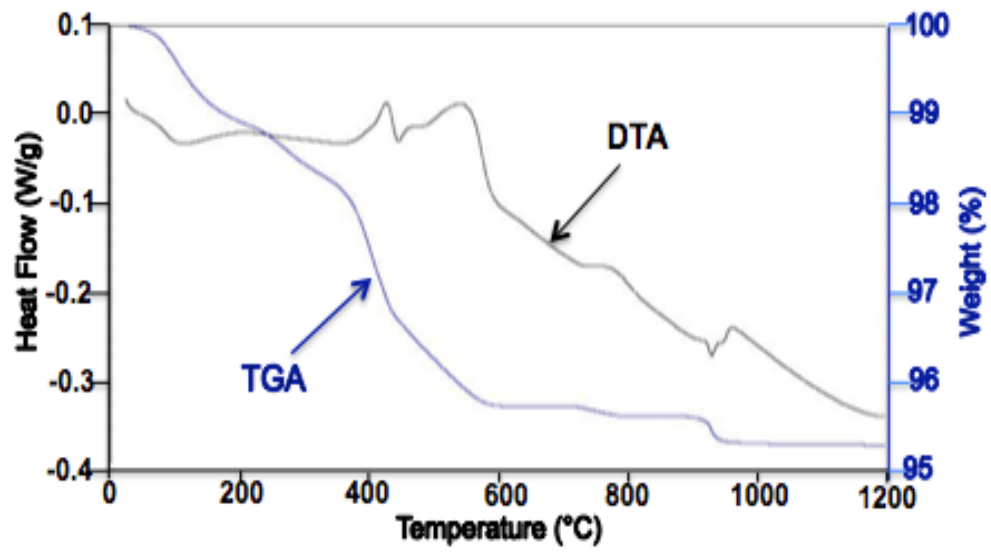


Figure 9. Schematic of data obtained during Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis.

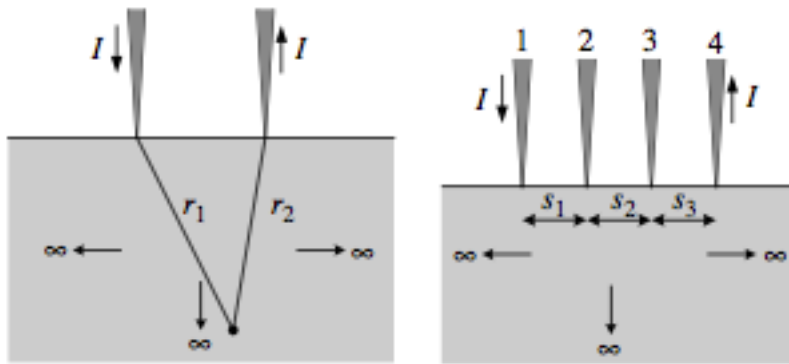


Figure 10. Schematics of (a) a two-point and (b) collinear four-point probes (Shrodingier [20]).

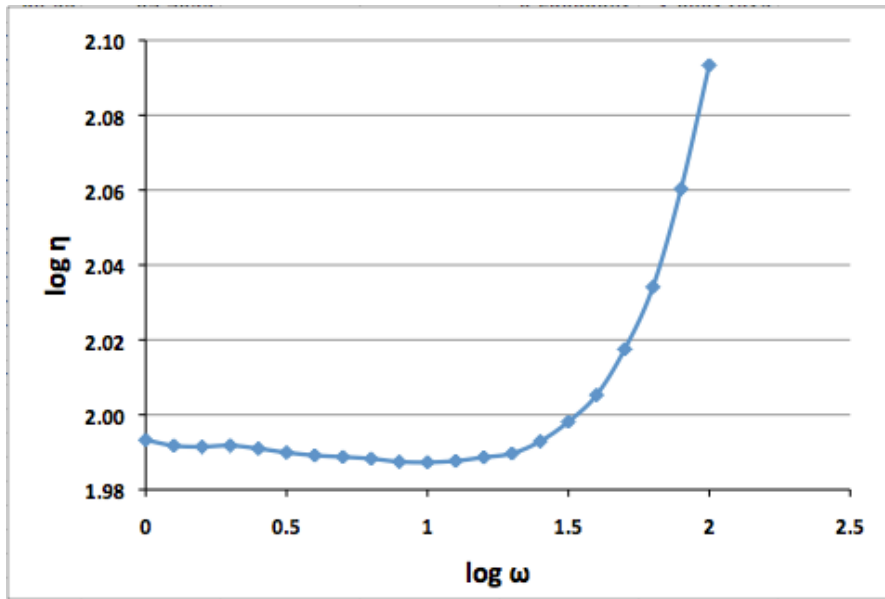


Figure 11. Log-log plot of viscosity versus frequency.

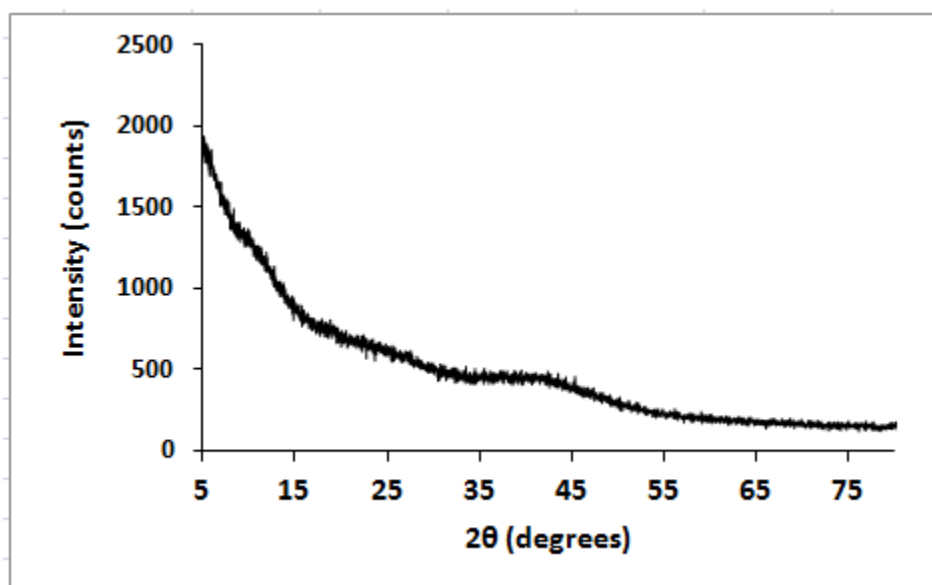


Figure 12. Room temperature x-ray diffraction data obtained from an unfired powder of mayenite.

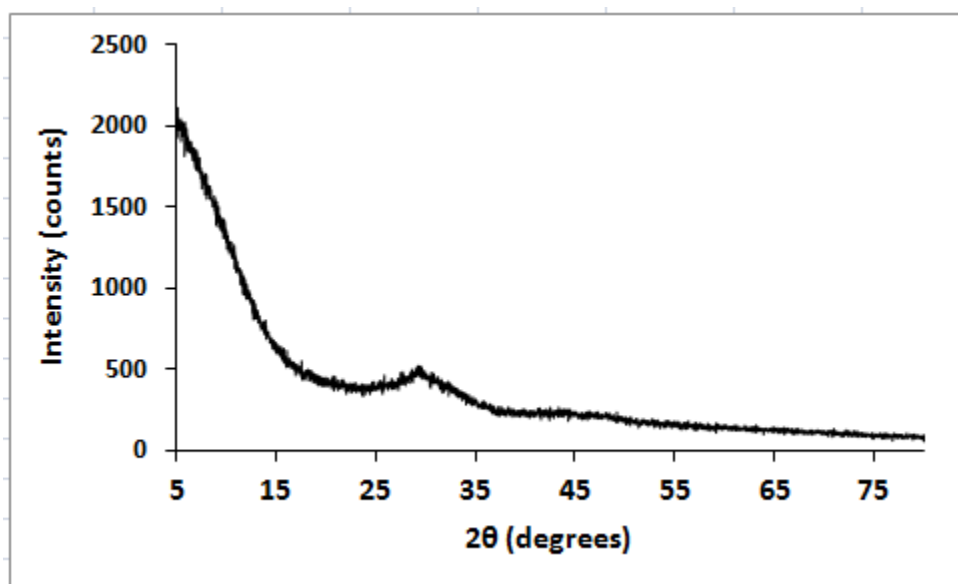


Figure 13. Room temperature x-ray powder diffraction data obtained from mayenite powder precalcined at 650 °C for one hour.

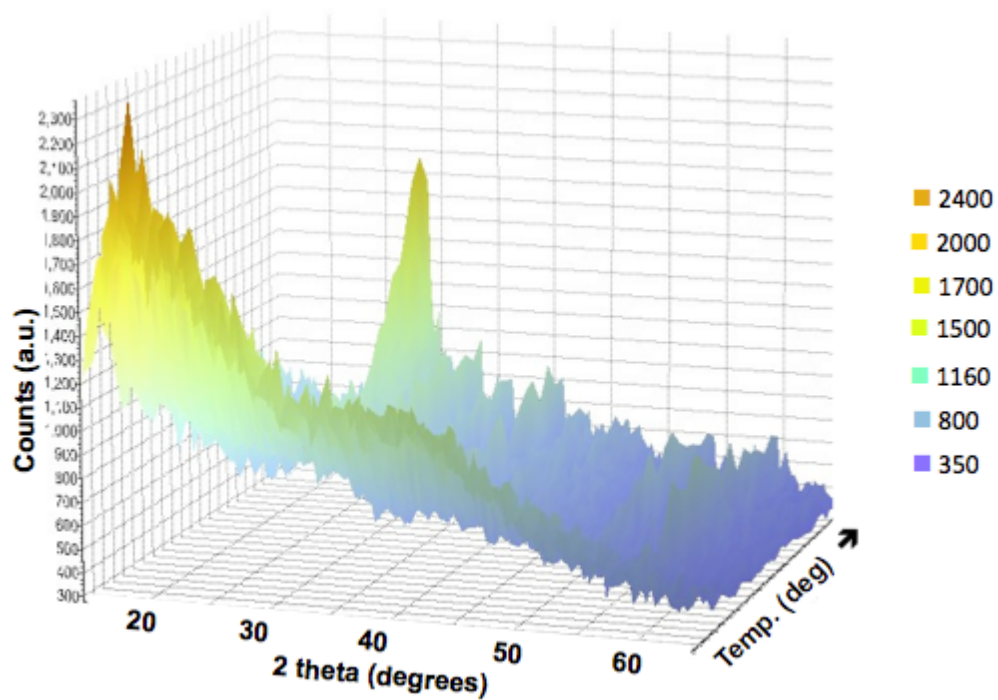


Figure 14. X-ray diffraction data collected between 100 – 875 °C in air.

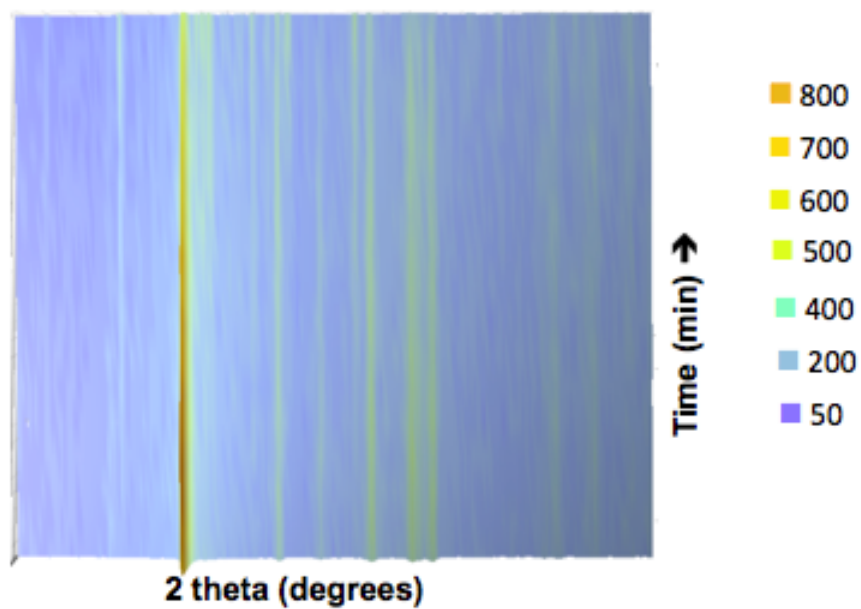


Figure 15. X-ray diffraction data collected at 850 °C in air on the mayenite sample pre-calcined at 650 °C showing only CaCO_3 .

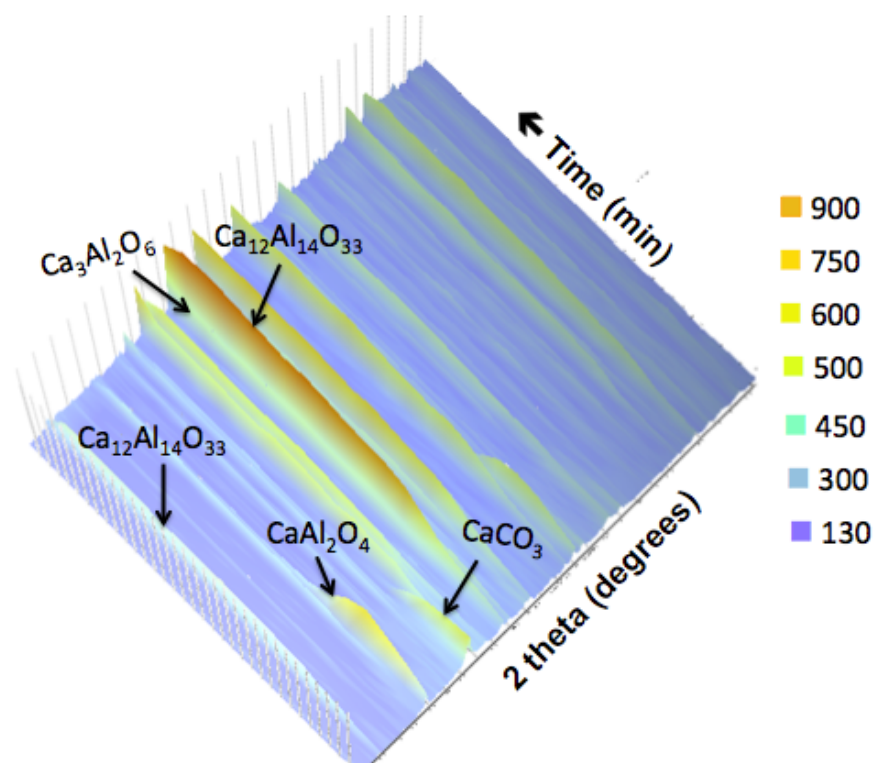


Figure 16. X-ray diffraction data collected at 875 °C in air on the mayenite sample pre-calcined at 650 °C.

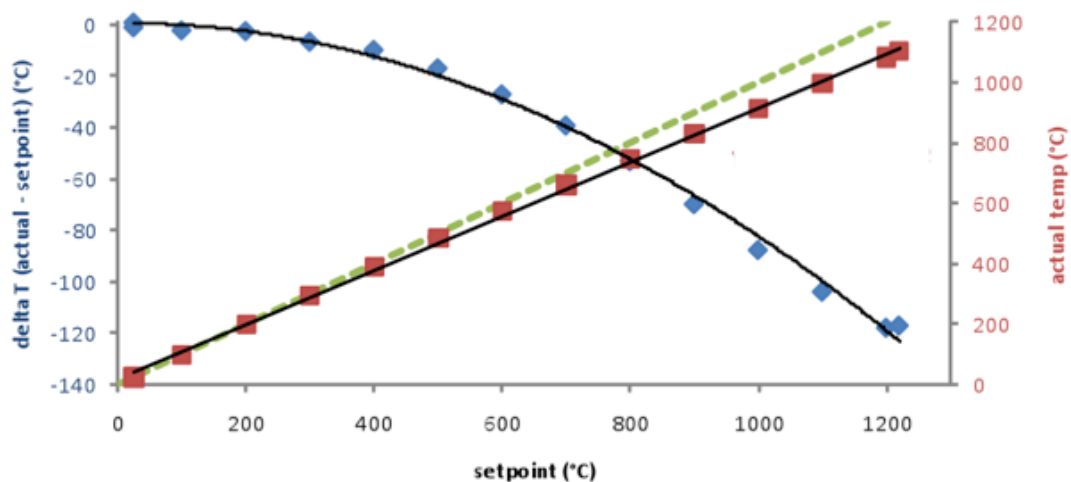


Figure 17. Temperature difference observed in MgO standard. Calculated temperatures (right axis, red), difference between the calculated and set point temperatures (left axis, blue), where set point would equal calculated temperature (green dashed line).

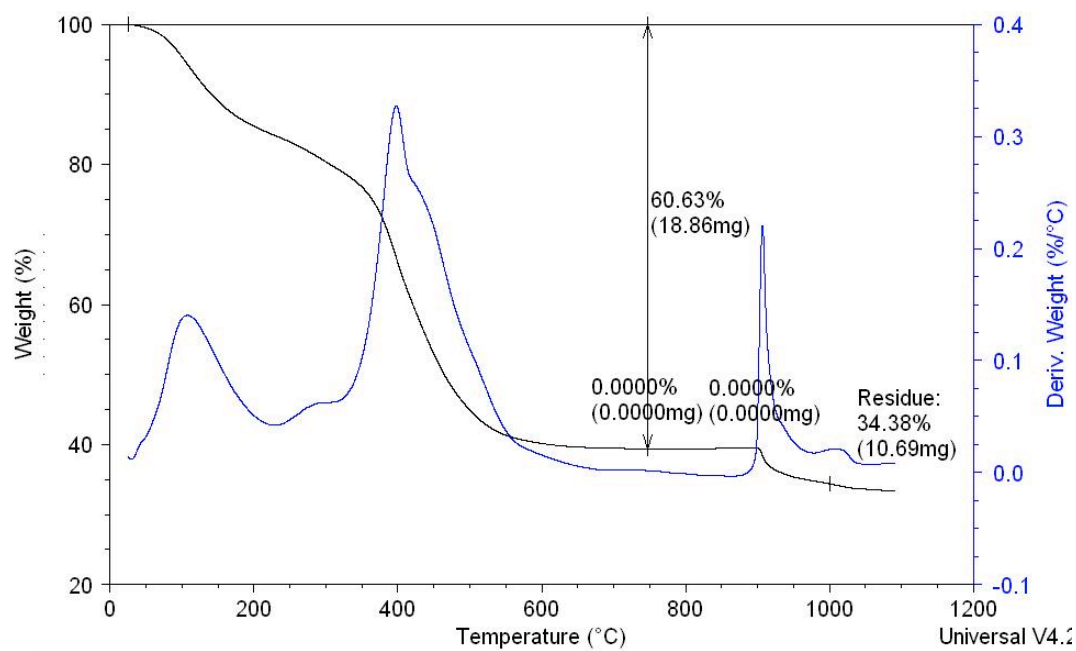


Figure 18. Thermo-gravimetric data collected on mayenite synthesized using citrate gel method. Data were collected in an Ar environment.

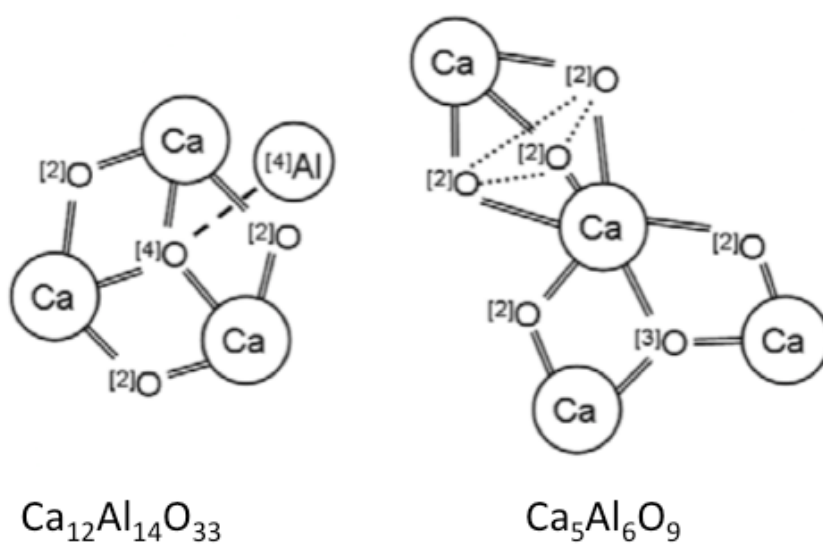


Figure 19. Ca Polyhedra of crystalline $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, and $\text{Ca}_5\text{Al}_6\text{O}_9$ (Adapted and modified from Vincent M. G. and Jeffery J. W. [31]).

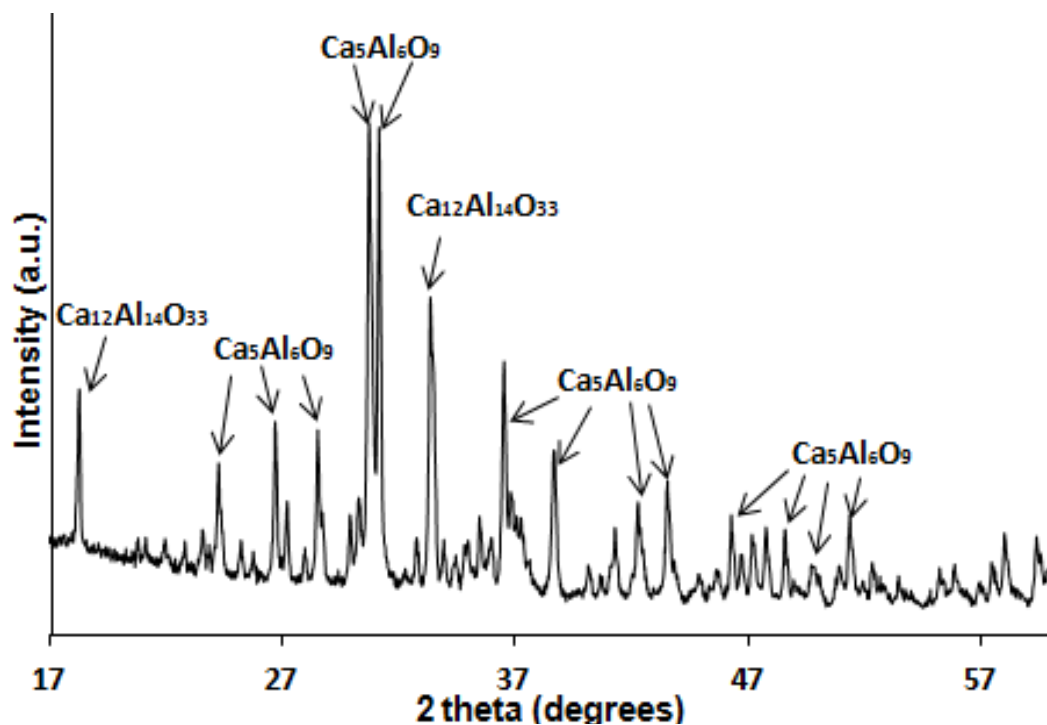


Figure 20. X-ray diffraction data collected on mayenite prepared with the reduced amount of citric acid and fired ex-situ in air at 1100 °C for 3 hours.

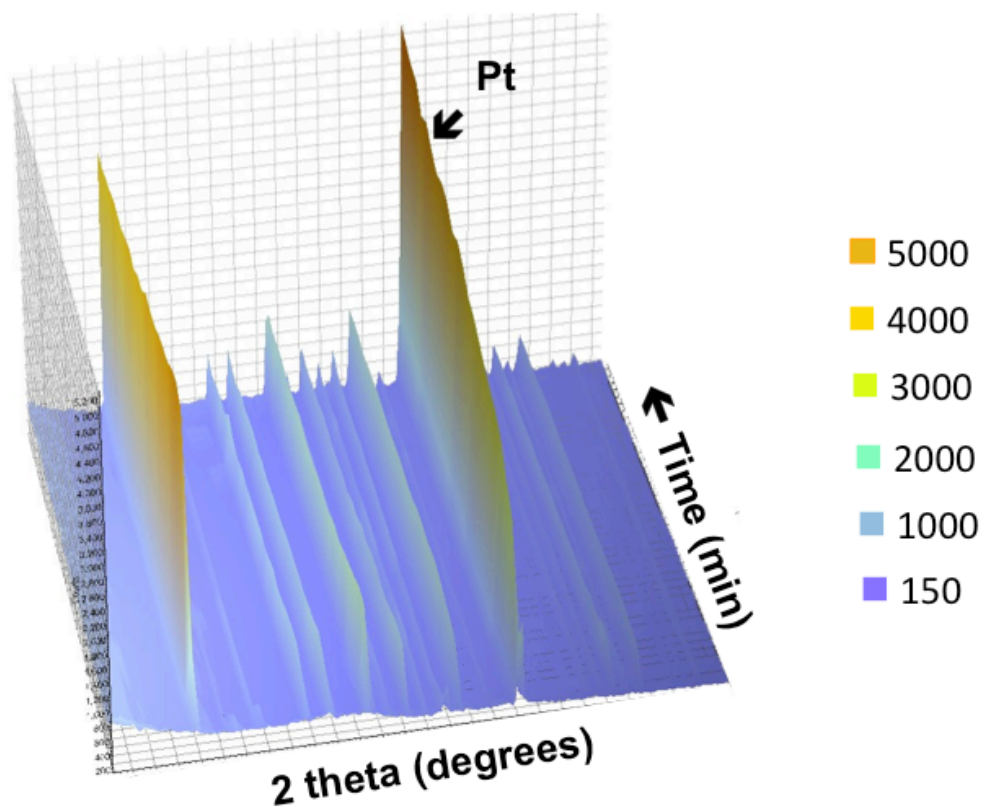


Figure 21. Time dependent X-ray diffraction data collected on the sample synthesized with $\frac{1}{2}$ mole% citric acid and fired at 900 °C.

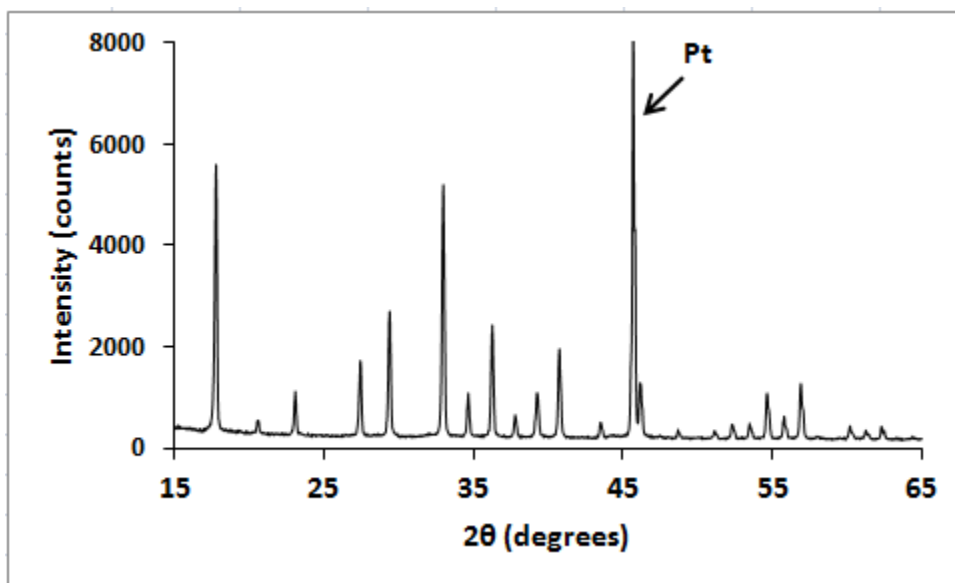


Figure 22. X-ray diffraction data collected on the sample synthesized with $\frac{1}{2}$ mole% citric acid and fired at 900 °C, at 40 minutes showing single phase mayenite. The observed Pt peak is from the strip heater.

Tables

Table 3. Bound Coherent Neutron Scattering Lengths of some elements [11].

Elements	Scattering length (fm)
Ca	4.80
Al	3.45
Fe	9.94
O	5.81
Ti	-6.08
¹ H	-3.74
² H	6.67

Table 4. Set and Calculated temperatures for Al₂O₃ standard.

Set Temperature (°C)	Calculated Temperature (°C)
650	510
900	711
1000	775

Table 5. Set and calculated temperatures for MgO standard.

Set Temperature (°C)	Calculated Temperature (°C)
919	850
979	900
1039	950
1100	1000
1161	1050
1224	1100

Table 6. Set and reference temperature readings and identified phases for K₂SO₄ standard.

Set Temperature (°C)	Reference Temperature (°C)	Identified Phases
580	410	Orthorhombic
590	417	Orthorhombic
600	423	Orthorhombic
610	430	Orthorhombic
620	437	Orthorhombic
700	491	Hexagonal
800	630	Hexagonal
620	491	Hexagonal
600	476	Hexagonal
25	22	Orthorhombic

Table 7. Set temperature, temperature determined from the optical pyrometer, and the reference temperature.

Set Temperature (°C)	Pyrometer Reading (°C)	Reference Temperature (°C)
919	810	650
979	825	685
1039	850	660
1100	905	684
1161	940	893
1214	1055	1004

Table 8. Identified phases at 810, 825, 850, 905, 940 and 1055 °C fired in air at 2, 40, 80, and 120 min. Temperatures are based on optical pyrometer readings. Refined wt %'s are given in parentheses.

Tem p. (°C)	2 min	40 min	80 min	120 min	Room Temperature, post firing
810	CaCO ₃ , CaAl ₂ O ₄	CaCO ₃ , CaAl ₂ O ₄ , Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	CaCO ₃ , CaAl ₂ O ₄ Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	CaCO ₃ , CaAl ₂ O ₄ , Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ (63.9%), Ca ₃ Al ₂ O ₆ (10.8%), CaAl ₂ O ₄ (25.3%)
825	CaCO ₃ , Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ (93.8%) CaAl ₂ O ₄ (6.2%)
850	Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆ , CaAl ₂ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ (100%)
905	Ca ₁₂ Al ₁₄ O ₃₃ , CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ 3, CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ (100%)
940	Ca ₁₂ Al ₁₄ O ₃₃ , CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆	Ca ₁₂ Al ₁₄ O ₃₃ 3, CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆ , Ca ₅ Al ₆ O ₉	Ca ₁₂ Al ₁₄ O ₃₃ 3, CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆ , Ca ₅ Al ₆ O ₉	Ca ₁₂ Al ₁₄ O ₃₃ 3, CaAl ₂ O ₄ , Ca ₃ Al ₂ O ₆ , Ca ₅ Al ₆ O ₉	Ca ₁₂ Al ₁₄ O ₃₃ (89%), Ca ₅ Al ₆ O ₉ (11%)
1055	Ca ₁₂ Al ₁₄ O ₃₃	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₅ Al ₆ O ₉	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₅ Al ₆ O ₉ , Pt ₃ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ 3, Ca ₅ Al ₆ O ₉ , Pt ₃ O ₄	Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₅ Al ₆ O ₉ , Pt ₃ O ₄ .

Table 9. Identified phases at 800, 850, 900, 950 and 1000 °C fired in 4% H₂/96% N₂ at 10 and 60 min. Temperatures are based on optical pyrometer readings.

Temperature (°C)	10 min	60 min
800	Amorphous	Amorphous
850	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (86.4%), Ca ₅ Al ₆ O ₉ (11.4%), Ca ₃ Al ₂ O ₆ (2.1%)
900	Ca ₁₂ Al ₁₄ O ₃₃ (87.6%), Ca ₅ Al ₆ O ₉ (11.5%), Ca ₃ Al ₂ O ₆ (0.9%)	Ca ₁₂ Al ₁₄ O ₃₃ (85.8%), Ca ₅ Al ₆ O ₉ (11.4%), Ca ₃ Al ₂ O ₆ (2.7%)
950	Ca ₁₂ Al ₁₄ O ₃₃ (89.0%), Ca ₅ Al ₆ O ₉ (10.0%), Ca ₃ Al ₂ O ₆ (1.0%)	Ca ₁₂ Al ₁₄ O ₃₃ (88.8%), Ca ₅ Al ₆ O ₉ (10.6%), Ca ₃ Al ₂ O ₆ (0.6%)
1000	Ca ₁₂ Al ₁₄ O ₃₃ (89.9%), Ca ₅ Al ₆ O ₉ (10.1%)	Ca ₁₂ Al ₁₄ O ₃₃ (82.7%), Ca ₅ Al ₆ O ₉ (11.8%), Ca ₃ Al ₂ O ₆ (5.4%)

Table 10. Compared properties between $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and $\text{Ca}_5\text{Al}_6\text{O}_9$

Parameters	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	$\text{Ca}_5\text{Al}_6\text{O}_9$
Crystal Structure	Cubic, nano-porous zeolite-like structure	Orthorhombic gehlenite-like structure
Space Group	I4-3d	Cmc2 ₁
Lattice Constant(s) (Å)	a = 11.97 – 12.02 with	a = 11.253, b = 10.966, c = 10.290
Formula units (Z)	2	4
Melting Temp (°C)	1380 -1415	1450 - 1455
Density (g/cm ³)	2.6 -2.9	3.1
Optical Properties	Transparent Color: colorless Optical class: isotropic. Refractive index, n =1.614 - 1.643	n = 1.683

Table 11. Phases present determined by XRD on samples after firing in various atmospheres and temperatures.

Experiment	Environment	Sample containment	Temp (°C)	Phases (wt%)
In-situ XRD	4% H ₂ /96% N ₂	Pt strip	1200	Ca ₁₂ Al ₁₄ O ₃₃ (51.1%), Ca ₅ Al ₆ O ₉ (48.9%)
DTA	Ar	Al ₂ O ₃ crucible	1100	Ca ₁₂ Al ₁₄ O ₃₃ (7.3%), Ca ₅ Al ₆ O ₉ (92.7%)
DTA (Re- fired in air)	Air	Al ₂ O ₃ crucible	1100	Ca ₁₂ Al ₁₄ O ₃₃ (50.8%), Ca ₅ Al ₆ O ₉ (49.2%)

Table 12. Phases identified by XRD in samples prepared with a reduced amount of citric acid.

Temperature (°C)	10 min	60 min
800	CaCO ₃ (100%)	CaCO ₃ , (17.7%), Ca ₃ Al ₂ O ₆ (1.2%), CaAl ₂ O ₄ (81.1%)
850	Ca ₃ Al ₂ O ₆ (14.1%), CaAl ₂ O ₄ (22.4%), Ca ₁₂ Al ₁₄ O ₃₃ (63.4%)	Ca ₃ Al ₂ O ₆ (13.4%), CaAl ₂ O ₄ (24.3%), Ca ₁₂ Al ₁₄ O ₃₃ (56.5%), Ca ₅ Al ₆ O ₉ (5.8%)
900	Ca ₃ Al ₂ O ₆ (5.8%), CaAl ₂ O ₄ (18.5%), Ca ₁₂ Al ₁₄ O ₃₃ (70.4%), Ca ₅ Al ₆ O ₉ (5.4%)	Ca ₁₂ Al ₁₄ O ₃₃ (98.5%), Ca ₅ Al ₆ O ₉ (1.5%)
950	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (100%)
1000	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (100%)
1050	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (100%)
1100	Ca ₁₂ Al ₁₄ O ₃₃ (96.8%), Ca ₅ Al ₆ O ₉ (3.2%)	Ca ₁₂ Al ₁₄ O ₃₃ (97.1%), Ca ₅ Al ₆ O ₉ (2.9%)

Table 13. Phases identified by XRD in samples prepared with a full mole % of citric acid.

Temperature (°C)	10 min	60 min
800	CaCO ₃	CaCO ₃ (11.6%), CaAl ₂ O ₄ (37.5%), Ca ₁₂ Al ₁₄ O ₃₃ (50.9%)
850	Ca ₁₂ Al ₁₄ O ₃₃ (73.9%), CaCO ₃ (1.3%), Ca ₃ Al ₂ O ₆ (11.7%), Ca ₅ Al ₆ O ₉ (1.3), CaAl ₂ O ₄ (11.8%)	Ca ₅ Al ₆ O ₉ (13.1%), Ca ₁₂ Al ₁₄ O ₃₃ (29.5%), CaAl ₂ O ₄ (30.8%), Ca ₃ Al ₂ O ₆ (26.6%)
900	Ca ₅ Al ₆ O ₉ (13.5), Ca ₁₂ Al ₁₄ O ₃₃ (39.3%), Ca ₃ Al ₂ O ₆ (21.2%), CaAl ₂ O ₄ (26.0%)	Ca ₅ Al ₆ O ₉ (7.4%), Ca ₁₂ Al ₁₄ O ₃₃ (87.5%), Ca ₃ Al ₂ O ₆ (5.1%)
950	Ca ₅ Al ₆ O ₉ (0.7%), Ca ₁₂ Al ₁₄ O ₃₃ (97.5%), Ca ₃ Al ₂ O ₆ (1.9%)	Ca ₁₂ Al ₁₄ O ₃₃ (96.2%), Ca ₃ Al ₂ O ₆ (3.2%)
1000	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (97.2%), Ca ₃ Al ₂ O ₆ (2.8%)
1050	Ca ₁₂ Al ₁₄ O ₃₃ (89.6%), Ca ₃ Al ₂ O ₆ (10.4%)	Ca ₁₂ Al ₁₄ O ₃₃ (98.4%), Ca ₃ Al ₂ O ₆ (1.6%)
1100	Ca ₁₂ Al ₁₄ O ₃₃ (100%)	Ca ₁₂ Al ₁₄ O ₃₃ (100%)

Table 14. Refined lattice parameters used to calculate the coefficient of thermal expansion of mayenite.

Temperature (°C)	Lattice constant (Å)
27	11.981(1)
900	12.0580(4)
950	12.0626(4)
1000	12.0666(4)
1050	12.0710(4)
1100	12.076(1)

CHAPTER II
HIGH TEMPERATURE X-RAY STUDIES OF MAYENITE
SYNTHESIZED USING CITRATE SOL-GEL METHOD

Disclosure

This chapter is based on the manuscript prepared for the journal *Ceramics International*. The full list of authors includes Sabina N. Ude, Claudia J. Rawn, Roberta A. Peascoe, Gregory L. Jones; Melanie J. Kirkham, E. Andrew Payzant. Sabina Ude performed all experiments, processed and analyzed all data, and prepared the manuscript for submission. Roberta Peascoe, Melanie Kirkham, and E. Andrew Payzant assisted with the data collection of the XRD and HTXRD data. Gregory Jones assisted with the Scanning Electron Microscopy studies included in the manuscript. Claudia Rawn assisted with the data analysis. Claudia Rawn, Melanie Kirkham, and E. Andrew Payzant assisted with contributing to the writing and editing of the manuscript.

Abstract

A citrate sol-gel method has been used to synthesize mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$). X-ray powder diffraction data show that the samples synthesized using the citrate sol-gel method contained CaAl_2O_4 and CaCO_3 along with mayenite when fired ex-situ in air at 800 °C but were single phase when fired at 900 °C and above. Using high temperature x-ray diffraction, data collected in-situ in air at temperatures of 600 °C and below showed only amorphous content; however, data collected at temperatures above 600 °C indicated the first phase to crystallize is CaCO_3 . High temperature x-ray diffraction data collected in 4%

H₂/96% N₂ does not show the presence of CaCO₃, and Ca₁₂Al₁₄O₃₃ starts to form around 850 °C. DTA/TGA data collected either in a nitrogen environment or air on samples synthesized using the citrate gel method suggest the complete decomposition of metastable phases and the formation of mayenite at 900 °C, although the phase evolution is very different depending on the environment. Brunauer-Emmett-Teller (BET) measurements showed a slightly higher surface area of $7.4 \pm 0.1 \text{ m}^2/\text{g}$ in the citrate gel synthesized samples compared to solid-state synthesized sample with a surface area of $1.61 \pm 0.02 \text{ m}^2/\text{g}$. SEM images show a larger particle size for samples synthesized using the solid-state method compared to those synthesized using the citrate gel method. Digital optical microscopy was used to evaluate a film of mayenite deposited on a sapphire substrate and fired at 1100 °C.

Keywords: Transparent Conductive Oxide, High Temperature X-ray Powder Diffraction B, Citrate sol-gel synthesis A, Scanning Electron Microscopy

Introduction

The mineral mayenite (Ca₁₂Al₁₄O₃₃), historically studied as a common phase present in Portland cement, has recently enjoyed renewed research interest due to the discovery of oxygen mobility [1-4], ionic conductivity [5-8], and catalytic properties [9, 10]. The physical properties observed in mayenite are related to its crystal structure. The crystal structure is cubic with a unit cell edge of

approximately 12 Å and has Z (formula units) of 2 [5] and is comprised of both nano-pores and polyhedra that form cages (similar to zeolites). The formula $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ refers to a unique feature of the anion diffusion process, 64 of the 66 oxygen ions per unit cell are fixed in a Ca-Al-O framework forming 12 “cages”[11], while the other two oxygen ions are distributed within the cages, the formula can be written as in equation 3-1 below.



The cages are approximately 5 Å in diameter and the openings between them are approximately 3.5 Å. It has been suggested that these openings control the mass transport between the inner cages and the outside [11]. On average each cage has a mean effective charge of +1/3. The free oxygen anions compensate for this positive charge of the framework and are loosely bound to the framework. There is flexibility for the substitution of the free O^{2-} ions with other anions such as fluoride, chloride, hydroxides or hydride, as well as electrons, forming electrides [2, 12-17]. Another application, in addition to being an electride, is the generation of negative O^- used in chemical syntheses and materials modifications [18, 19].

Mayenite has been prepared in various ways, with solid-state synthesis being the commonly used method. Wet chemistry routes are becoming popular especially

sol-gel synthesis. Sol-gel technique involves the conversion of a solution of molecular precursors by a chemical reaction into a sol or a gel, which is subsequently transformed into a crystalline material upon drying and firing [20]. Synthesis steps are performed under ambient conditions, involving no difficult technical challenges in terms of instrumentation or special environment. Furthermore, it ensures adequate and homogenous mixing of the raw materials, and the produced gel can easily be deposited as thin film on a substrate. In this work, citrate sol-gel method, which is simple and cost-effective, has been used to prepare bulk mayenite at a temperature of 900 °C in about three hours.

Materials and Methods

Synthesis

The starting materials for the solid-state synthesis were powders of CaCO_3 (Fisher Chemicals, 99%) and $\gamma\text{-Al}_2\text{O}_3$ (Alfa Aesar, 99.5%). The powders were appropriately weighed out and thoroughly mixed with an agate mortar and pestle, using methanol. After drying the powder was pressed into a pellet using a 13 mm die. The pellet was fired in an alumina crucible at 1200 °C for 16 hours, and then reground in the agate mortar and pestle, re-pressed, and fired at 1350 °C for 23.5 hours then air quenched. The starting materials for the citrate gel technique included $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fisher Chemical, 99.5%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fisher Chemical, 98.9%), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Alfa Aesar, 99%). The citric acid is a type of weak alpha-hydroxycarboxylic acid that has the ability to form polybasic

acid chelates with various cations [21]. This ensures cations are uniformly distributed in the mixture. Appropriate amounts of nitrates were measured and dissolved in de-ionized water; the solution was heated on a hot plate up to 60 °C before adding the citric acid. The citrate-nitrate mixture was heated and vigorously stirred with magnetic stir bar at 90 °C until a gel was formed (about 4-7 hours). The resulting gel was placed in a drying oven slightly above 100 °C to dry off the H₂O, and the gel transformed into a cake-like structure, which was subsequently crushed into powder using an agate mortar and pestle. The powder was then divided for the ex-situ and in-situ firings. The samples for the ex-situ experiment were pressed into four pellets. The pellets were each fired at various temperatures (T = 1100, 1000, 900 and 800 °C) for 4 hours in alumina crucibles. All samples were air quenched and ground by hand in the agate mortar and pestle for subsequent phase identification using x-ray powder diffraction. The powder for the in-situ experiments was pre-calcined at 450°C or 600 °C. Chart 1 in appendix C illustrates the steps of the citrate gel synthesis.

Characterization

X-ray powder diffraction was used to characterize the resulting powders. The data were collected on a PANalytical X'Pert PRO MPD θ - θ diffractometer equipped with an X'celerator Real Time Multiple Strip (RTMS) detector that allows ultrafast data collection. The system was operated at 45 kV and 40 mA using Cu K α radiation. The data were collected over a range of 10° - 75° 2 θ with

a 0.017° step size and a count time set so that each data collection lasted approximately 12 minutes. Data for Rietveld refinements were collected using longer count times. An Anton Paar HT16 environmental chamber with a platinum strip heater was used for the in-situ studies. Due to thermal gradients along the strip where both ends of the strip heater are water-cooled, and thermal gradients between the sample and the strip due to interfacial thermal contact resistance between the sample and the strip, as well as contributions due to the thermal conductivity of the sample, a temperature calibration was performed using Al₂O₃ and MgO standards to verify the accuracy of the temperature readings. Additionally, an optical pyrometer was used to determine the temperature of the powder during the study. Data were collected in both air and flowing 4% H₂/96% N₂. Quantitative phase amounts were determined from Rietveld refinements performed using the EXPGUI graphical interface [22] for the General Structure Analysis System (GSAS) [23]. Jade [Jade 6.0, Materials Data Inc.] and HighScore plus [*X'Pert HighScore Plus 3.0, PANalytical, Inc.*] software packages were used for phase identification.

Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) were conducted using a TA Instruments SDT Q600 (simultaneous TGA/D`SC) at a rate of 5°C/min with either N₂ or compressed air as the purging gas. A digital optical microscope (Keyence Digital Microscope, VHX – 1000) was used to examine the dispersion and thickness of citrate gel prepared mayenite powder deposited on a sapphire substrate. The powder was made into suspension by

mixing with ethylene glycol and was deposited on the substrate using a pipette. It was dried over night in a drying oven above 100 °C and then fired at 1100 °C for 1 h. X-ray diffraction data of the film was collected before and after firing to monitor any change in structure. Scanning Electron Microscopy (SEM) analysis was conducted on the solid-state sample fired at 1350 °C and the citrate gel sample fired at 1100 °C. Micrographs were collected using a LEO 1525 Field Emission Scanning Electron Microscope. Specific surface area and porosity were measured on samples prepared by solid-state method, and samples prepared by citrate gel method and fired at 800, 900, and 1100 °C using a Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer.

Results and Discussion

Physical Properties

Qualitative physical properties of the pellets after firing included changes in size and color. As expected the pellet size decreased, with the citrate gel generated samples showing a significant reduction in size due, in part, to the loss of evolved gaseous compounds such as NO₂, CO₂, NO, etc. The decrease in weight was confirmed by the thermo-gravimetric analysis results presented in Figure 23a, with about 34 wt% of the sample remaining after the analysis. All samples synthesized using the citrate gel technique and fired in air were white after firing at temperatures above 800°C, and the sample fired at 800°C was grey suggesting that at this temperature the sample did not reach equilibrium. Firing

the pellets in a reducing atmosphere resulted in a black color. The citrate gel samples were easier to grind by hand compared to the solid-state samples.

Thermal Analysis

The TGA/DTA data collected on mayenite, synthesized using the citrate gel method, in a N_2 environment are shown in Figure 23a. Three areas of major weight changes are observed. The first peak is at approximately 100 °C resulting from the evaporation of water; the second peak is at approximately 400 °C, possibly resulting from the decomposition of the nitrates and burning off of other organic compounds, and the third peak is at approximately 900 °C suggesting the complete decomposition of all meta-stable phases and formation of mayenite. The DTA data collected on mayenite synthesized using the citrate gel method, in air, are shown in Figure 23b and show a more complicated reaction. Water evaporates above 100 °C followed by decomposition of citric acid around 175 °C. $Al(NO_3)_3$ decomposes into Al_2O_3 and NO_2 around 400 °C, while $Ca(NO_3)_2$ decomposes into CaO and NO_2 around 561 °C. The exothermic peak around 750 °C indicates the transition of an amorphous to a crystalline phase, this was also observed in the x-ray diffraction results which confirmed the crystalline phase to be $CaCO_3$. The peaks below and above 900 °C suggest decomposition of $CaCO_3$ initially formed from CO_2 from the citric acid and CaO from calcium nitrate, and complete decomposition of all meta-stable phases and formation of mayenite.

Ex-situ XRD

Figure 24 compares the ex-situ x-ray powder diffraction data for citrate gel samples fired in air and shows that all samples are single phase except for the sample fired at 800 °C. Ex-situ x-ray powder diffraction data collected on the citrate sol-gel sample fired in air at 800 °C showed a high background suggesting the presence of amorphous content. Crystalline phases present included $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (64.9 wt%), CaAl_2O_4 (21.9 wt%) and CaCO_3 (13.2 wt%). These results were determined without taking into consideration any amorphous phase. After re-firing at 800 °C in air for 4 h, the x-ray data collected showed a lower background and changes in the fractions of each phase, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (79.6 wt%), CaAl_2O_4 (14.0 wt%) and CaCO_3 (6.4 wt%) confirming that several firings at that temperature are necessary to reach equilibrium. The ex-situ x-ray powder diffraction data, collected on the samples synthesized by the citrate gel method and fired in air at 900 °C and above, all showed single-phase mayenite indicating that the approximate minimum temperature to obtain a single phase is 900 °C

In-situ XRD

Figure 25a compares the in-situ x-ray powder diffraction data for citrate gel samples at room temperature, 600, 750 and 800 °C. In-situ x-ray diffraction data collected in air at temperatures of 600 °C and below show only amorphous content; however, data collected at higher temperatures indicate the first phase to crystallize is CaCO_3 around 750 °C (confirmed from the DTA result), while the alumina content remains amorphous. Figure 25b shows in-situ x-ray data

collected at 850 °C over time. At 850 °C, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 are present. The CaAl_2O_4 phase disappeared over time leaving mayenite (99.1 wt%) as the dominant phase with a minor amount of $\text{Ca}_3\text{Al}_2\text{O}_6$ (0.9 wt%) present. Figure 26 compares in-situ x-ray powder diffraction data of citrate gel synthesis samples when in 4% H_2 / 96% N_2 at 800, 850 and 900 °C. Data collected in 4% H_2 /96% N_2 does not show the presence of CaCO_3 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is the first phase to form around 850 °C. At this temperature a minor amount of $\text{Ca}_5\text{Al}_6\text{O}_{14}$ was observed and the amount increased to 11.7 wt% when the temperature was at 900 °C. The $\text{Ca}_3\text{Al}_2\text{O}_6$ detected in samples fired in both air and 4% H_2 /96% N_2 is most likely due to slight errors of the starting ratios (e.g. possibly from excess H_2O in the precursors since the nitrates are hygroscopic).

Figure 27 shows the lattice parameters refined from the x-ray powder diffraction data collected on mayenite synthesized using the citrate sol-gel method and fired in-situ in air. The lattice constant was found to be 11.978(1) Å at room temperature, close to the literature value [5], and it increased linearly with increasing temperature. The linear thermal expansion coefficient was calculated from the refined lattice parameters to be $6.12 \times 10^{-6} \text{ K}^{-1}$ and is in good agreement with value reported by Boysen et al. [24].

Microscopy

X-ray powder diffraction data collected on the mayenite film deposited on the sapphire substrate showed no structural changes when compared to the data collected on the mayenite powder before deposition. However, the diffraction pattern collected after the deposition showed a minor extra peak, arising from the sapphire substrate, at around $2\theta = 42^\circ$. The diffraction pattern is shown in Figure 28 and the insert shows the peak from the sapphire substrate. The image of the deposited film under a digital optical microscope is shown in Figure 29a, while Figure 29b shows a topographical view of the film with one end showing a cross-sectional view for thickness determination. From the image the thickness of the film is determined to be below $200\text{ }\mu\text{m}$.

Figure 30 and Figure 31 show SEM images collected at different magnifications for the solid-state and citrate sol-gel samples, respectively. The micrographs show randomly shaped particles from samples synthesized using both techniques, however, particles produced using the citrate sol-gel technique were more rounded than the particles produced using solid-state synthesis. The particles produced using the citrate sol-gel technique were smaller and displayed more collapsed and smaller pores compared to particles produced using the solid-state synthesis.

Surface Analysis

The results of BET surface area analysis of solid-state and citrate gel synthesized samples are summarized in Table 15. A pore size of 34.39 nm and a surface area of 1.61(2) m²/g were determined for the sample produced using solid-state synthesis and fired at 1350 °C. In comparison, a pore size of 7.99 nm and a surface area of 2.99(4) m²/g were determined for the sample produced using the citrate sol-gel technique and fired at 1100 °C. It has been established that solid-state synthesis does not produce mayenite with high surface area [25], and the low surface area reported for the citrate sol-gel produced samples (i.e. less than 10 m²/g) suggests that this technique is not producing mayenite with a high surface area either. Instead, it was observed that the surface area decreased as the temperature increases regardless of the synthesis route, with the sample fired at 800 °C showing the maximum surface area of 7.4(1) m²/g. The decrease in the surface area could be attributed to collapse of the pores in the samples, which occurs with an increase in the temperature.

Conclusions

High temperature x-ray diffraction data collected on samples synthesized using the citrate gel technique in-situ in air at temperatures of 600 °C and below showed only amorphous content; however, data collected at higher temperatures indicated the first phase to crystallize is CaCO₃ and when fired in air at 800 °C showed multiple phases (Ca₁₂Al₁₄O₃₃, CaAl₂O₄ and CaCO₃) were present. When

fired ex-situ at 900 °C or above, x-ray powder diffraction data showed single-phase mayenite. In contrast high temperature x-ray diffraction data collected in 4% H₂/96% N₂ does not show the presence of CaCO₃, and Ca₁₂Al₁₄O₃₃ starts to form around 850 °C. DTA/TGA data support unique phase evolution paths for the two different environments. Particles produced by the citrate gel method show more and smaller pores compared to particles synthesized using the solid-state technique, however, BET surface area analysis shows that the citrate gel synthesis does not produce mayenite with high surface area. Citrate sol-gel synthesis proves to be a good technique for producing mayenite requiring less time and lower temperatures, without subsequent firings in order to reach equilibrium.

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Department of Energy. The authors would like to thank Austin Albert for his help with the BET data collection and analysis.

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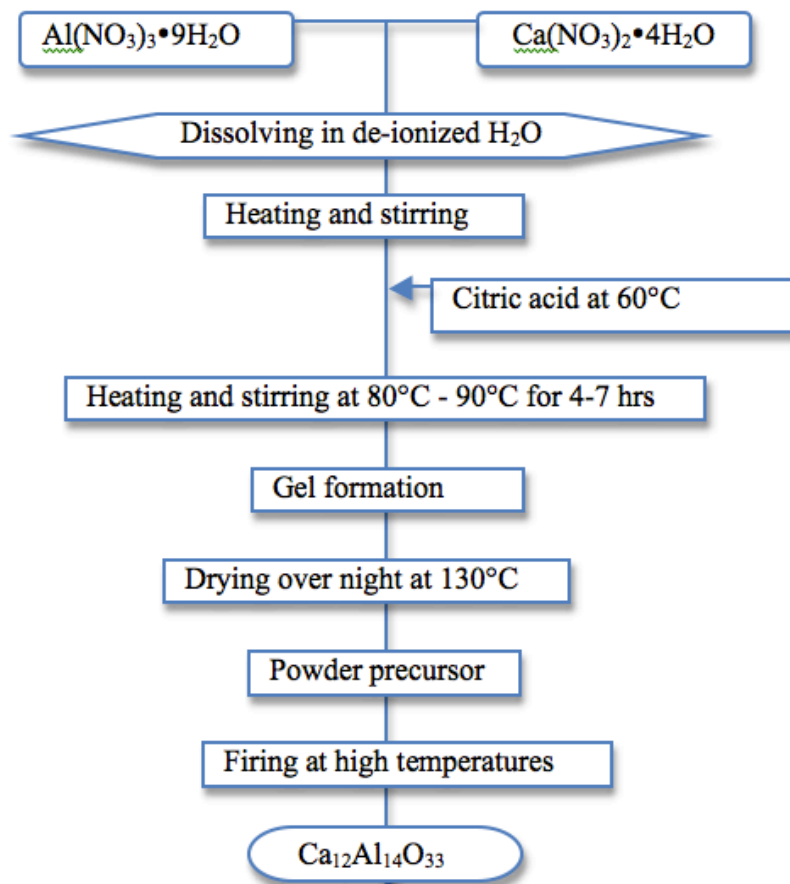
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Appendix C

Chart

Chart 1. Flow chart of the citrate gel synthesis of mayenite.



Figures

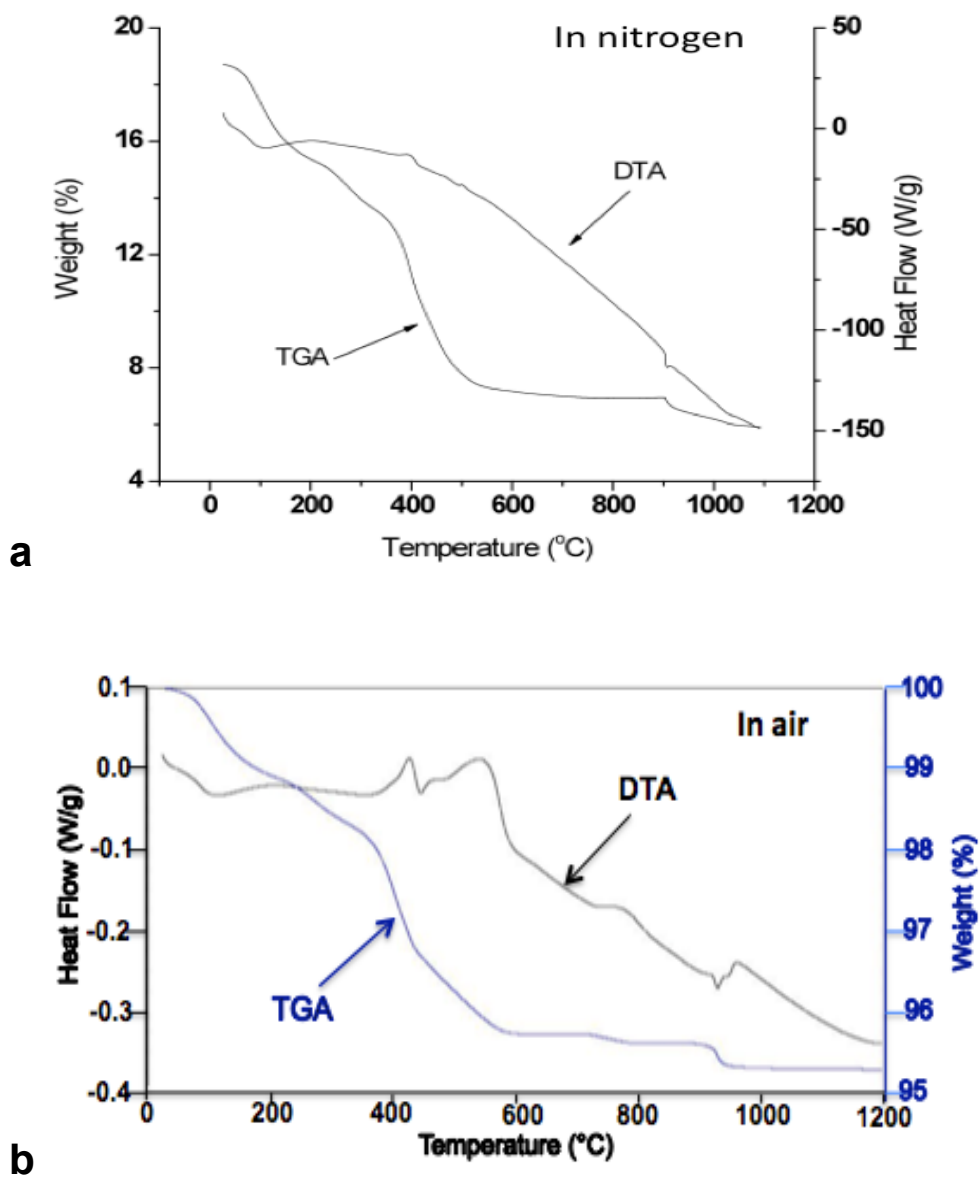


Figure 23. DTA/TGA curves of mayenite synthesized using the citrate gel method collected in (a) a N_2 environment and (b) compressed air environment.

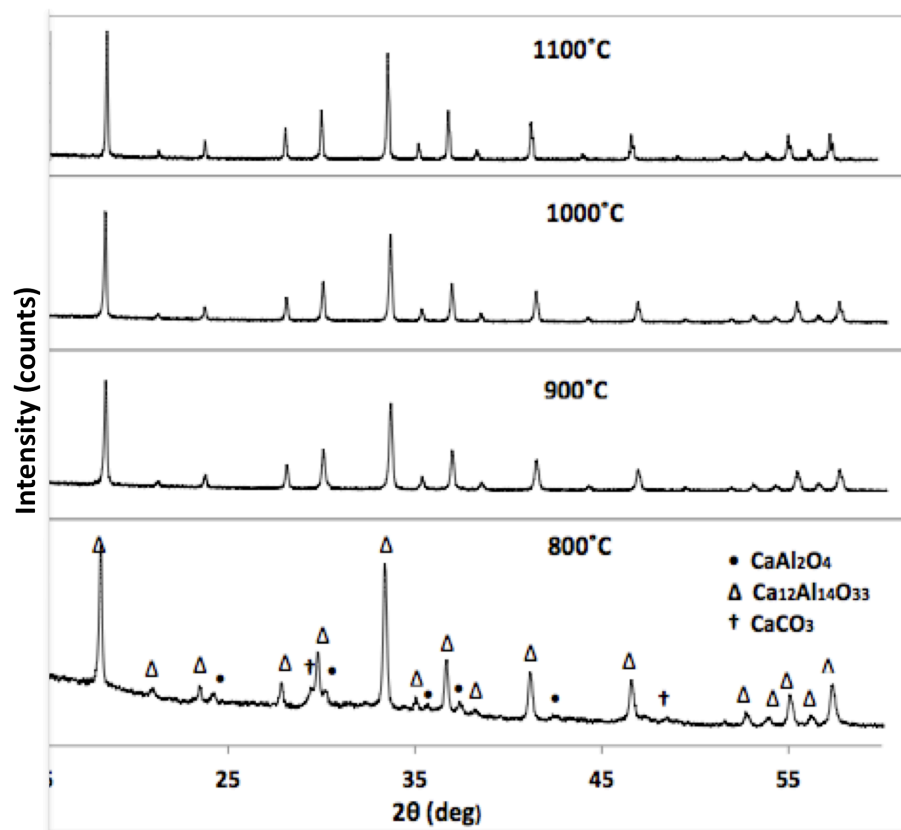


Figure 24. Ex situ x-ray powder diffraction pattern collected on mayenite synthesized using the citrate gel method and fired in air at 800, 900, 1000, or 1100 °C.

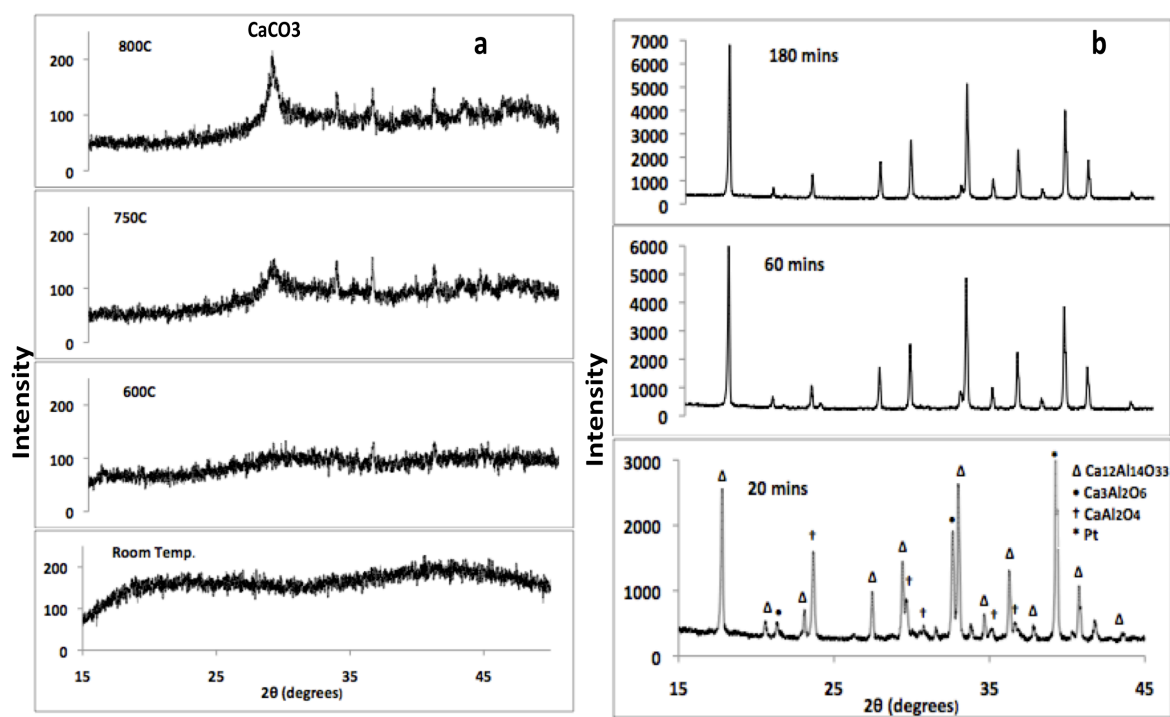


Figure 25. In-situ x-ray powder diffraction pattern of mayenite synthesized using the citrate gel method, fired in air (a) at room temperature, 600, 750 and 800 °C, and (b) at 850 °C over time.

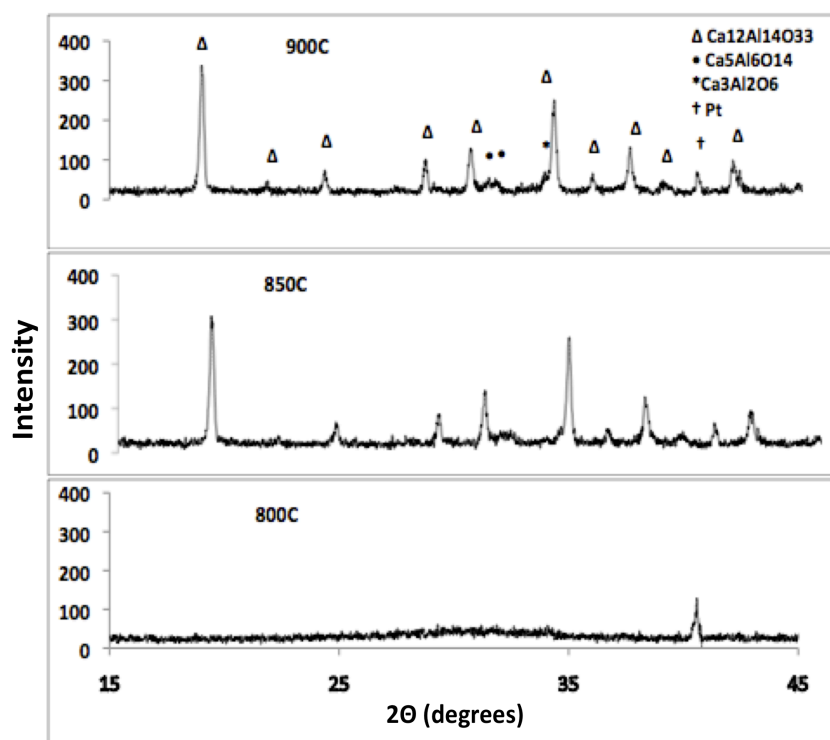


Figure 26. X-ray powder diffraction pattern of mayenite synthesized using the citrate gel method and fired in 4% H₂/96% N₂ at 800, 850 and 900 °C.

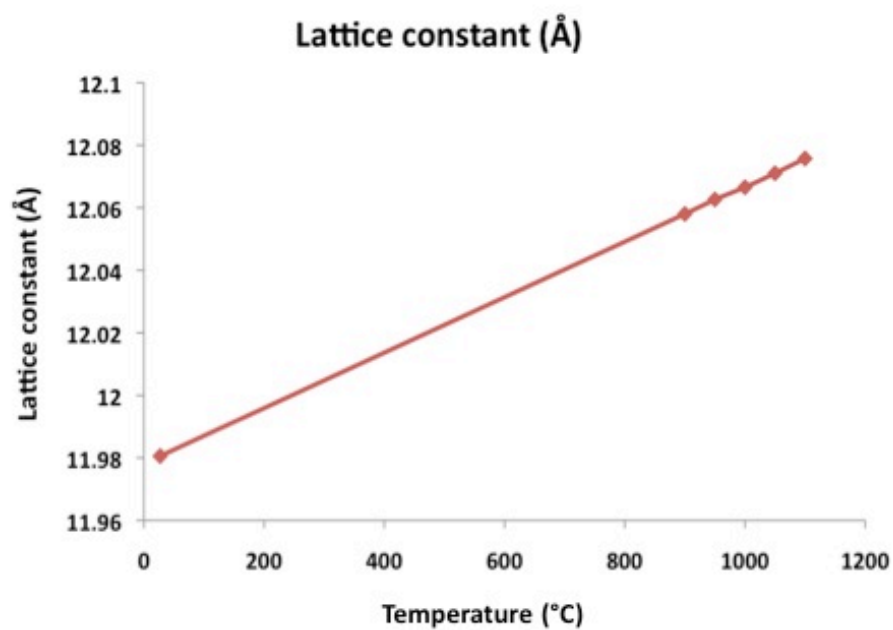


Figure 27. Refined lattice parameters of mayenite synthesized using the citrate gel method versus temperature.

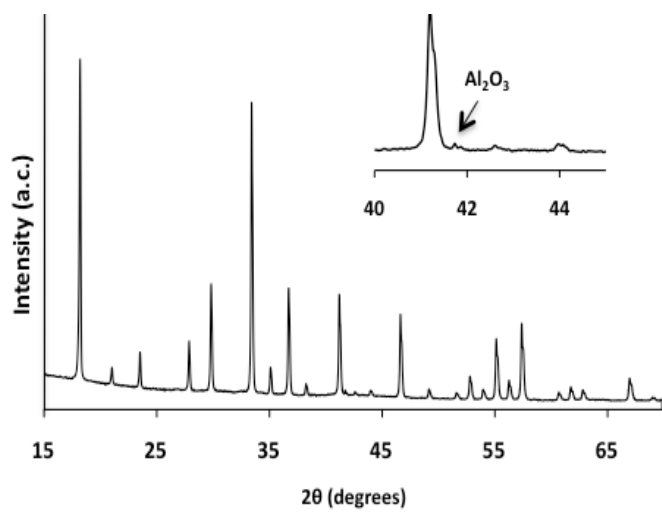


Figure 28. X-ray powder diffraction pattern of mayenite film deposited on a sapphire substrate.

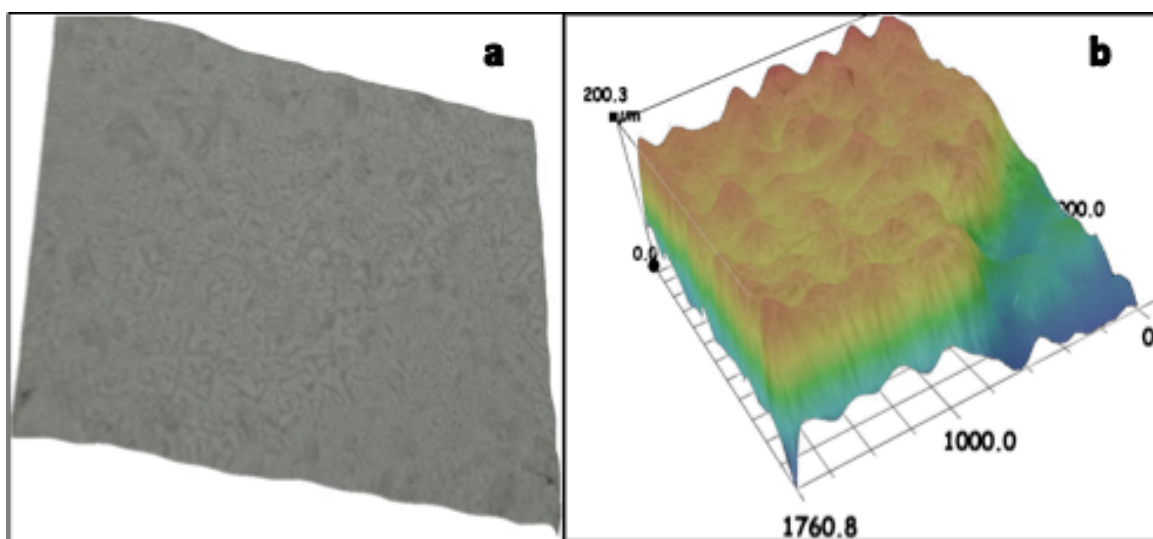


Figure 29. Digital optical images of deposited mayenite film on sapphire substrate (a) plan view and (b) topographical view.

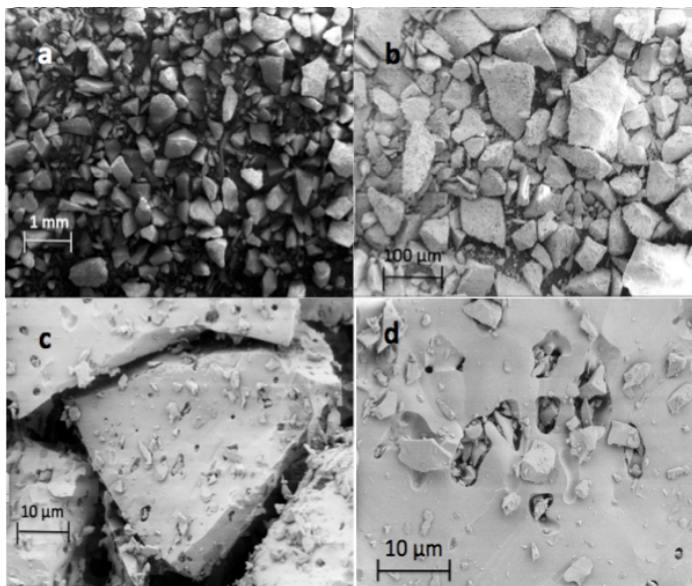


Figure 30. SEM micrographs of solid-state synthesized mayenite fired at 1350 °C and taken at (a) 50X, (b) 100X, (c) 500X, and (d) 2500X.

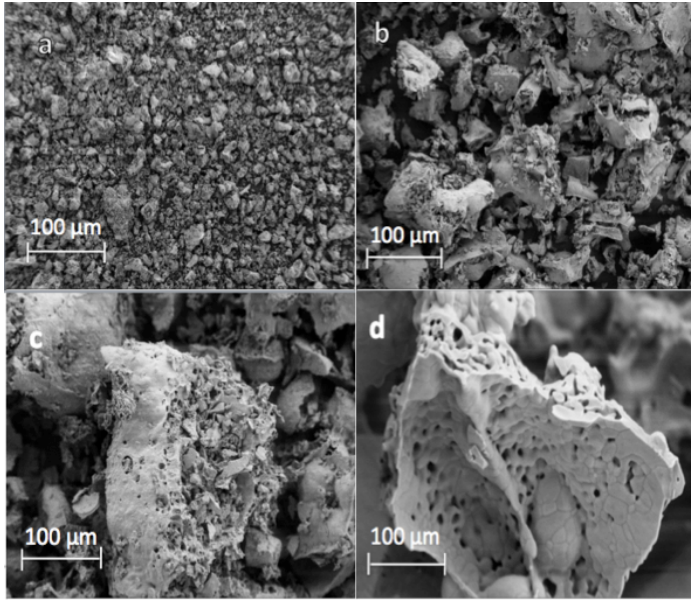


Figure 31. SEM micrographs of citrate gel synthesized mayenite fired at 1100 °C and taken at (a) 100X, (b) 500X, (c) 1000X, and (d) 20000X.

Table

Table 15. Summary of BET results.

Technique	Temperature (°C)	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Citrate gel	1100	2.99 ± 0.04	0.006	7.99
Citrate gel	900	6.1 ± 0.2	0.069	44.81
Citrate gel	800	7.4 ± 0.1	0.083	44.71
Solid state	1350	1.61 ± 0.02	0.014	34.39

CHAPTER III
THE SYNTHESIS AND CRYSTAL CHEMISTRY OF $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$
(MAYENITE) DOPED WITH FE

Disclosure

This chapter is based on the manuscript prepared for submission to a peer reviewed Journal. The full list of authors includes Sabina N. Ude, Claudia J Rawn, Ashfia Huq and Thomas T. Meek. Ashfia Huq collected the neutron data and Sabina Ude and Claudia Rawn analyzed neutron data. Sabina Ude synthesized the samples, collected the x-ray powder diffraction data and the 2-point probe resistivity data and processed and analyzed both the structural and electrical data. Thomas Meek assisted in analyzing the electrical measurements. Sabina Ude prepared the manuscript for submission and Claudia Rawn assisted with the writing and editing

Abstract

X-ray and neutron powder diffraction have been used to study the crystal chemistry of Fe doped mayenite ($\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$). Solid-state synthesis was used to prepare $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ where $x = 0, 0.1, 0.2, 0.5$ and 0.6 and the citrate gel route was used to prepare $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ where $x = 0, 0.05, 0.1, 0.2, 0.3$ and 0.4 . The X-ray powder diffraction data indicate that samples with the same composition but synthesized by the citrate gel route were more likely to be phase pure than samples obtained by traditional solid-state synthesis. The refined lattice parameters were observed to increase with increasing Fe concentration, irrespective of the synthesis method. Refined neutron powder data

suggest that Fe is going into Al site rather than Ca site. A 2-point probe was used to measure the electrical properties of the Fe doped citrate gel synthesized samples and showed that the resistivity increases for the Fe doped samples compared to the undoped mayenite.

Introduction

The mineral mayenite, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, has been traditionally known as a constituent of Portland cements. It crystallizes with a body centered cubic crystal structure belonging to the $I-43d$ (number 220) space group with $a = 11.989 \text{ \AA}$ with 2 formula units per unit cell [1]. In recent decades mayenite's interesting electrical, optical, and catalytic properties have been discovered [2-11]. These interesting physical properties result from its unique framework structure that allows various anions to be distributed among the cages formed by the framework [6, 12, 13].

Since many attractive physical properties are a result of point defects, it is of interest if cation substitutions can be made in the framework of mayenite and how these defects would affect the anion distribution inside the cages and ultimately the conductivity of mayenite. Will the conductivity change by introducing point defects replacing either Ca^{2+} or Al^{3+} by Fe^{2+} or Fe^{3+} and if so how much of the Ca and/or Al can be replaced by Fe? A ternary phase diagram of the $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system, shown in Figure 32, indicates there is a limited range of Fe incorporation into the mayenite structure [14]. Boysen et al. used

neutron powder diffraction to characterize samples with 0.1 and 2.5 mol% Fe synthesized by the sol-gel method, and indicated that doping mayenite with Fe suppressed the incorporation of extra anions while exhibiting large disorder in the crystal [15]. Boysen predicted high anionic conductivity due to an observed large disorder at room temperature and extreme delocalization at high temperatures; however, the effect of Fe on the electrical properties of mayenite has not been reported.

In this present work, pure and Fe substituted mayenite have been synthesized using both solid state and citrate gel techniques, and the resulting crystal structures characterized using x-ray and neutron powder diffraction. The electrical property has been measured using a 2-point probe.

Experimental

Fe doped samples, $\text{Ca}_{12-x}\text{Fe}_x\text{Al}_{14}\text{O}_{33}$, where $x = 0.1, 0.2, 0.3$ and 0.4 were prepared using solid-state synthesis, while another set of samples of Fe doped ($\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$) mayenite were produced by both solid-state and citrate gel syntheses. Starting powders of CaCO_3 (Fisher Chemicals, 99%), Al_2O_3 , (Alfa Aesar, 99.5%) and Fe_2O_3 (Alfa Aesar, 99.95%) were used as precursors for the solid-state synthesis where $x = 0, 0.1, 0.2, 0.5$ and 0.6 . The synthesis was carried out as described by Ude et al. [16]. The samples were initially fired at 1200°C for 16 hours. The final firing of the undoped mayenite was at 1350°C for

23.5 hours, while the Fe doped samples were fired at 1350 °C for 18 hours. To explore if the firing of Fe doped samples could be lowered samples where $x = 0.2$ and 0.6 were fired at 1200 and 1300 °C for 18 h.

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fisher Chemical, 99.5%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fisher Chemical, 98.9%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros, 98%) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Alfa Aesar, 99%) were used as precursors for the citrate gel synthesis where $x = 0, 0.05, 0.1, 0.2, 0.3$ and 0.4. The synthesis also followed the route as described by Ude et al. [16]. The resulting powder was divided in half and one half was used to press pellets and subsequently fired at 1000 °C for 4 h in air while the other half was pre-calcined at 600 °C as a loose powder and then pressed into pellets and fired in flowing 4% H_2 /96% Ar at 1200 °C for 6 h.

Samples used in x-ray and neutron diffraction measurements were ground into fine powders. For the x-ray powder diffraction measurements, the powders were back loaded into deep well sample holders and spun during the data collection to improve sampling statistics. The data were collected on a PANalytical X'Pert PRO MPD θ - θ diffractometer. The diffractometer was equipped with an X'celerator Real Time Multiple Strip (RTMS) detector that allows ultrafast data collection. The system was operated at 45 KV and 40 mA and data were collected using Cu $\text{K}\alpha$ radiation over a 2θ range of 5-140° with a count time set so that each data collection lasted approximately 20 minutes. X-ray powder diffraction data were analyzed using Jade [Jade 6.0, Materials Data Inc.] and

HighScore [X'Pert HighScore Plus 3.0, PANalytical, Inc.] software packages for phase identification; and Rietveld refinements were performed using the EXPGUI graphical interface [17] for the General Structure Analysis System (GSAS) [18].

Neutron powder diffraction data were collected on samples synthesized using the citrate gel method where $x = 0$ and 0.3 . The diffraction measurements were carried out using the high resolution powder diffractometer (POWGEN) at the Spallation Neutron Source at Oak Ridge National Laboratory [19]. Samples were loaded in 6 mm diameter V cans and data were collected at room-temperature, using wavelength bands centered at 1.066 and 1.599 Å covering a d spacing range of $0.3 - 4.3$ Å. Rietveld refinements on the collected data were performed using the GSAS software package and the EXPGUI interface.

Electrical resistance measurements were carried on a probe station using a 2-point probe. The measurements were from 0 to 20 V at a step size of 0.5 V and 0.1 compliance.

Results and Discussion

General physical observations of the pellets after firing included color changes. For both synthesis techniques the sample without Fe was white after firing in air compared to the samples containing Fe which were light green and became darker with increasing Fe content. Figure 33a shows an image of samples

synthesized using solid-state method where $x = 0.1$ and 0.6 . The samples prepared using citrate gel method and fired in flowing 4% $H_2/96\%$ Ar turned black, samples where $x = 0.1$ and 0.4 are shown in Figure 33b. As the Fe content was increased the samples were easier to grind. It has been noted that Fe increases the porosity in sinters thereby reducing their strength [20].

Phase Identification

X-ray powder diffraction data collected on the Fe doped samples, $Ca_{12-x}Fe_xAl_{14}O_{33}$, with Fe substituting on Ca site showed multiple phases. The identified phases were $Ca_{12}Al_{14}O_{33}$ and $CaAl_2O_4$ with the $CaAl_2O_4$ content increasing as Fe content increased. Samples where $x = 0.3$ and 0.4 contained a third phase, $Ca_2Fe_{0.7}Al_{1.3}O_5$. These results indicate that Fe does not replace Ca but rather Al in the solid solution. The identified phases are summarized in Table 16. Fe substitution on Al site will be discussed in detail later. The lattice constant was observed to increase with increasing Fe concentration.

Figure 34 compares the X-ray powder diffraction data for the $Ca_{12}Al_{14-x}Fe_xO_{33}$ samples prepared using the citrate gel route. Samples with $x = 0, 0.05, 0.1$, and 0.3 were single phase while the samples where $x = 0.2$ and 0.4 contained a minor amount (less than 0.1 wt%) of the meta-stable phase $Ca_5Al_6O_{14}$ present as a secondary phase. The double peaks belonging to $Ca_5Al_6O_{14}$ are seen at $2\theta =$

30.58 and 31.02°. $\text{Ca}_5\text{Al}_6\text{O}_{14}$ is a meta-stable phase whose production is favored in oxygen deficient environment and also by high temperature [21].

Figure 35 compares X-ray powder diffraction data for the $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ samples prepared using solid-state synthesis. Only the sample without Fe was single phase, all samples with Fe contained $\text{Ca}_3\text{Al}_2\text{O}_6$ as a secondary phase and their weight fractions are given in Table 17. The $\text{Ca}_3\text{Al}_2\text{O}_6$ major peak position is at $2\theta = 33.21^\circ$. The sample where $x = 0.5$ and 0.6 had small amounts of an extra phase in addition to $\text{Ca}_3\text{Al}_2\text{O}_6$ with two major peaks located at $2\theta = 45.5^\circ$ and 34.1° . The peaks from the extra phase were found to match the phase $\text{Ca}_2\text{Fe}_{0.7}\text{Al}_{1.3}\text{O}_5$ [22]. The presence of $\text{Ca}_2\text{Fe}_{0.7}\text{Al}_{1.3}\text{O}_5$ in both samples, suggests that incorporation of Fe beyond $x = 0.4$ cannot yield single-phase solid solution of mayenite. Furthermore, samples with $x = 0.2$ and 0.6 fired at various temperatures (1200, 1300 and 1350 °C) showed similar x-ray patterns for each Fe content at the various temperatures, proving that equilibrium can be reached at a lower temperature (1200 °C) when mayenite is doped with Fe as compared to 1350 °C when undoped.

Neutron Powder Diffraction

Figure 36 compares the lattice parameters, obtained from the Rietveld refinements of x-ray data, for the samples synthesized by both techniques. The mayenite structure reported by Bartl et al [23] was used as the model during

refinement. For both synthesis techniques the lattice parameter showed a slight increase with increasing Fe concentration. For coordination number of 6, the ionic radius for Al is 0.54, 0.65 for Fe and 1 Å for Ca. It will be easier for Fe to replace Al since their radii are closer compared to that of Ca. The increase in lattice parameter then suggests that Fe is replacing Al since Fe has larger ionic radius than Al. The defect reaction of Fe^{3+} in mayenite represented by Kroger-Vink notation would be as shown in equation 4-1 below. Also, the presence of the secondary phase $Ca_3Al_2O_6$ in some of the samples as Fe increase shows that the quantity of Al was decreasing while Ca is increasing as the reaction moves towards CaO rich region in the CaO – Al_2O_3 binary phase. Also, during refinement, with addition of Fe on Ca site, the *sof* was over 1 while that of Fe was negative, yet another evidence that Fe does not go into Ca site. This will be discussed in details with the neutron powder diffraction data.

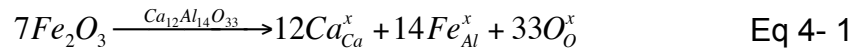


Figure 37 shows the neutron powder diffraction data (I_{obs}) collected at room temperature (298 K) for the citrate gel base mayenite ($x = 0$), the calculated neutron powder diffraction pattern (I_{calc}), and the difference pattern ($I_{obs} - I_{calc}$). The structure proposed by Bartl and Scheller [24], with only one Ca site (24*d*) and where the O atom located on the 24*d* site is only partially occupied, was first used to model the calculated pattern. Full refinement on both the atomic positions and atomic displacement parameters was not possible. Next the

structure proposed by Boysen et al. [24], with two partially occupied Ca atoms on different 24d sites and the O atom, that Bartl and Scheller [24] suggested was on the 24d site, was moved slightly to occupy a 12a site, was used to model the calculated pattern. The refinements using the two partially occupied Ca positions resulted in one of the Ca's atomic displacement parameters going non-positive definite, however, moving the O from the 24d site to the 12a site and having only one Ca position resulted in improved fit. A total of 36 variables were refined including all atomic positions, atomic displacement parameters, the site occupancy for the O on the 12a site and resulted in a $\chi^2 = 1.704$ ($R_{wp} = 4.8\%$ and $R_{exp} = 3.71\%$). Refining on the site occupancy factor (sof) of the O atom in the 12a site revealed the site was about $\frac{1}{4}$ occupied resulting in a chemistry of $\text{Ca}_{24}\text{Al}_{28}\text{O}_{67}$, slightly oxygen rich.

The samples were synthesized according to $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ indicating the Fe was substituting for the Al as suggested by Boysen [16]. To confirm this, neutron powder diffraction data were collected on a sample with $x = 0.3$. The calculated diffraction pattern was originally modeled with the one Ca position and the partially occupied O in the 12a position and then a series of additional patterns were calculated with the Fe in all of the different framework cation sites. Without adding Fe to the structure and refining on 34 variables including all the atomic positions and atomic displacement parameters resulted in a $\chi^2 = 1.593$ ($R_{wp} = 5.71\%$ and $R_{exp} = 4.55\%$). Next the site occupancy factors of all atoms were refined and resulted in a slightly lower χ^2 and statistically significant vacancies on

sites with the exception of the Al on the 16c site. Creating a model where the Ca and Fe shared a site and the atomic positions and the atomic displacement parameters were constrained to be equal, and refining on the site occupancies resulted in negative sof for Fe and a value greater than one for Ca and the refinement diverged. When Fe was placed on the Al sites separately the refinements did not diverge and slightly lower χ^2 s were obtained ($\chi^2 = 1.587$ when Fe replaced the Al on the 16c position and $\chi^2 = 1.592$ when Fe replaced the Al on the 12b site). Based on the refined compositions a more significant amount of Fe was located on the 16c position. Two additional refinements were attempted one with Fe substituting on both Al sites and one with Fe substituting on all three cation sites. Both of these refinements resulting in slightly lower but not significantly lower χ^2 s, especially given the fact that more variables were introduced using these models. Based on all these refinements it appears that Fe is substituting on to the Al 16c site, however the calculated formula based on the refinement results was slightly low in Al and high in Fe. For the samples with $x = 0$ and $x = 0.3$ the refined lattice constants were $a = 11.9884(3)$ and $11.9934(3)$ Å, respectively, agreeing with the results determined from refinements on the x-ray powder diffraction data.

Conductivity Results

A graph of resistance versus voltage of the measured samples is shown in Figure 38. The undoped sample showed a resistance of about $1.0 \times 10^6 \Omega$, which

was fairly constant at increased voltage. The contact resistance arising between the metal probe and the sample may have contributed to the somewhat high resistance observed in this sample. This is usually the case when using a 2-point probe. However, when compared to the Fe doped samples, they showed even higher resistance, which linearly increases with the voltage. It is assumed that the higher resistance observed in the Fe doped samples is as a result of mobile electrons being trapped by the oppositely charged impurity centers created by Fe. The crystal structure of mayenite consists of a positively charged framework $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}$ and free oxygen O^{2-} distributed randomly within the cages of the framework to maintain the charge neutrality of the entire crystal. When the free oxygen ions are removed from the cages through reduction process, electrons are introduced to the cages to keep the charge neutrality of the crystal. These electrons bring about conductivity and conductivity changes from ionic to metallic as the electron concentration goes from low to high. But in a case where a dopant creates a dopant center or well that is deep, the electrons became electro-statically bound to these centers and become immobile. This is assumed to be the reason why the Fe doped samples showed higher resistance when compared to the undoped sample.

Conclusions

Fe was introduced into mayenite using both solid-state and citrate gel syntheses. Samples prepared using citrate gel were able to incorporate more Fe while

maintaining phase purity while solid-state samples showed multiple phases. It was observed that beyond 0.4 atomic %, Fe started to precipitate out. The lattice parameter of mayenite was observed to increase with increased Fe content as a result of the larger ionic radius in Fe than the Al it is replacing. There was a decrease in conduction from the undoped to the doped mayenite, suggesting that Fe is not an appropriate dopant in enhancing the electrical properties of mayenite.

Acknowledgement

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APPENDIX D

Figures

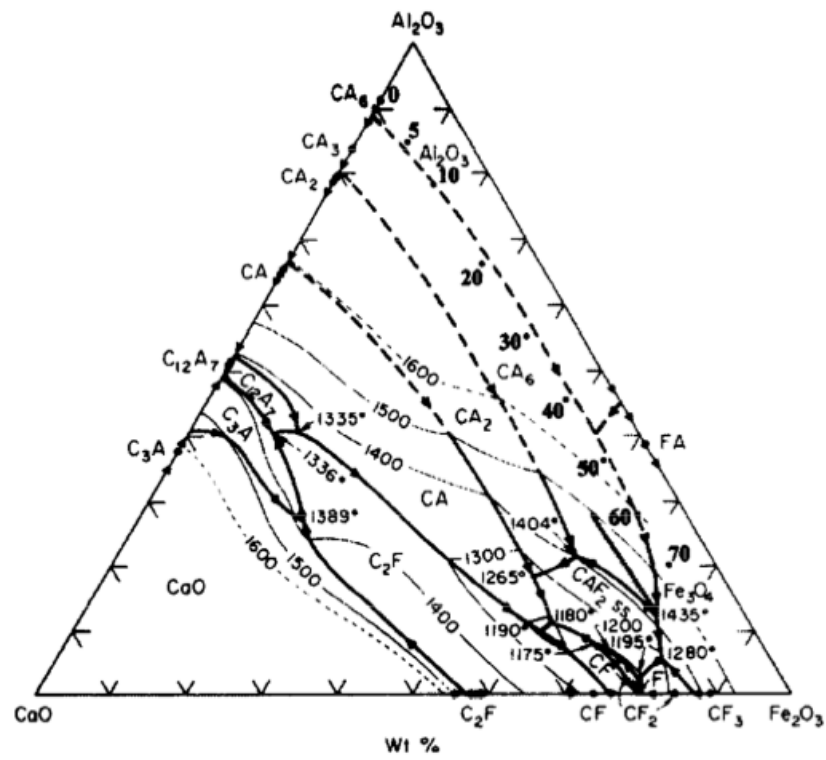


Figure 32. CaO-Al₂O₃-Fe₂O₃ ternary phase diagram [14].

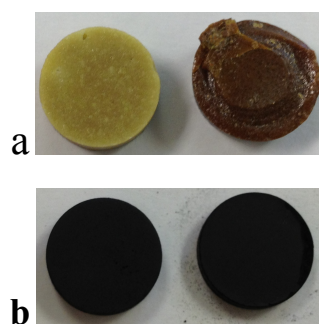


Figure 33. Images of $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ where (a) $x = 0.1$ (left) and 0.6 (right) synthesized using solid state techniques and fired in air and (b) $x = 0.1$ (left) and 0.4 (right) synthesized using citrate gel techniques and fired in $4\% \text{H}_2/96\% \text{Ar}$.

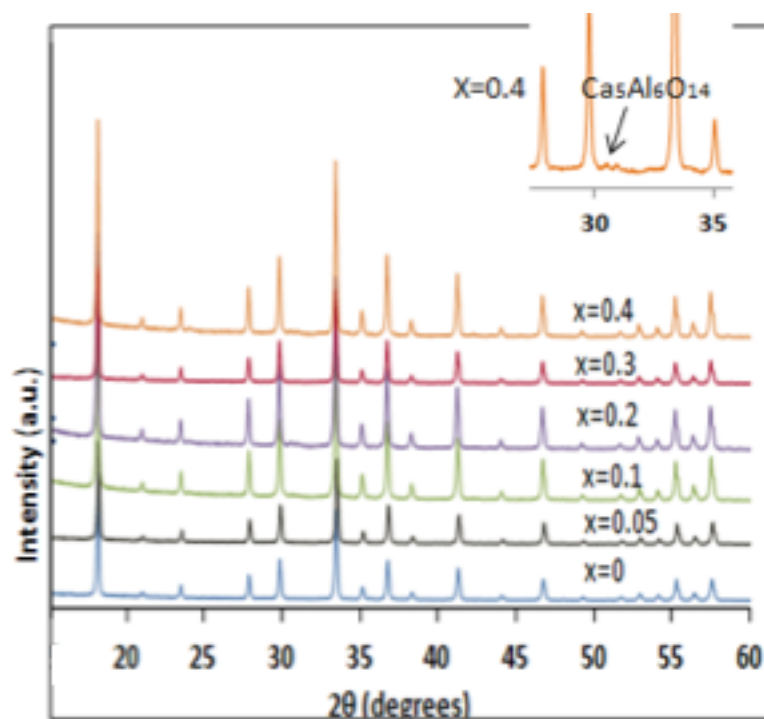


Figure 34. Powder X-ray diffraction data of $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ synthesized using the citrate gel method and fired at 1000 °C.

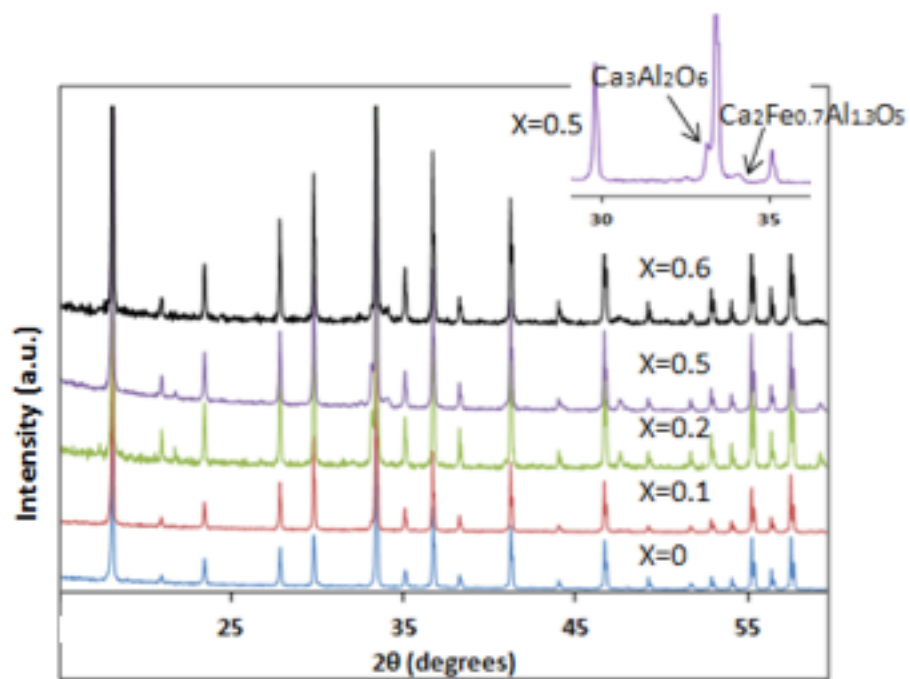


Figure 35. X-ray powder diffraction data of $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ synthesized by solid-state techniques.

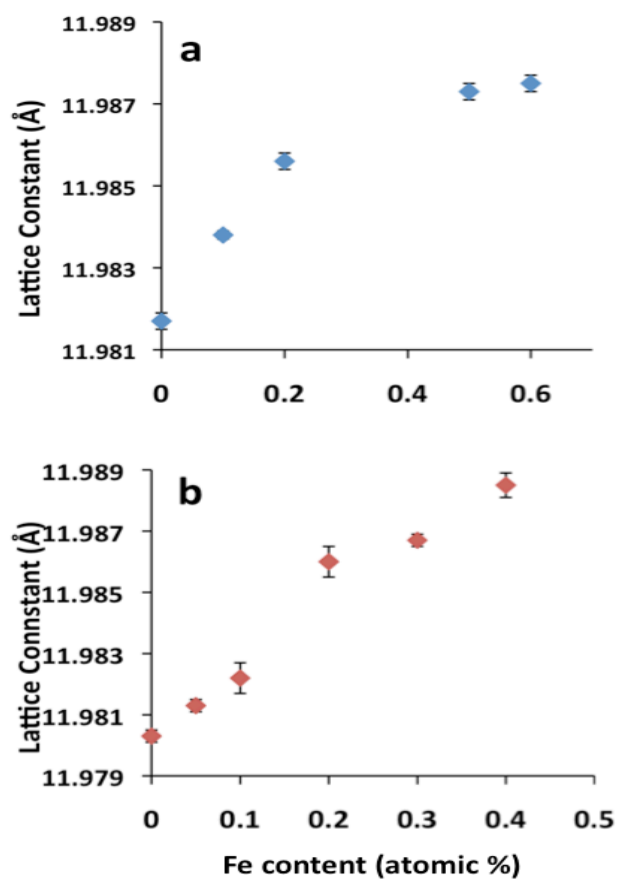


Figure 36. Lattice constant versus $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ where x = the Fe content for (a) solid state and (b) sol-gel samples.

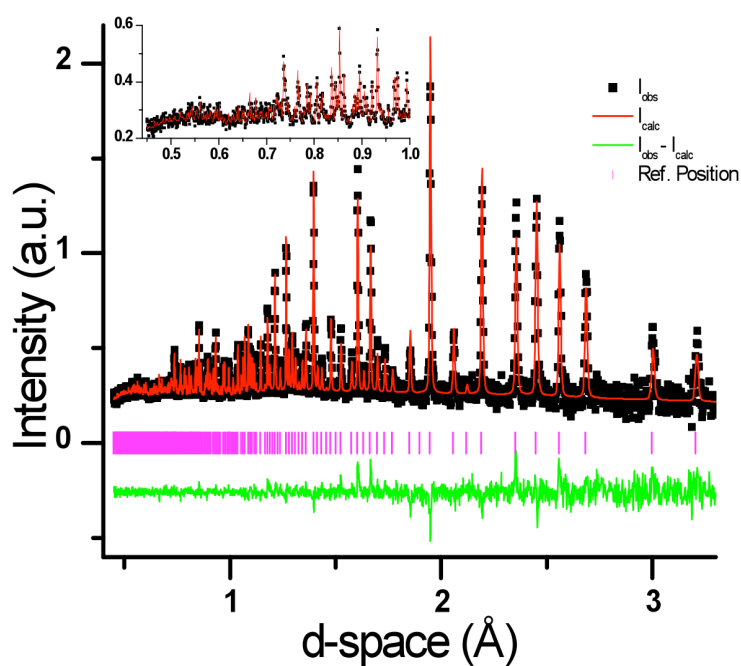


Figure 37. Observed neutron power diffraction data along with the neutron diffraction pattern calculated from the pure mayenite structure and POWGEN instrument parameters. The difference between the patterns is shown below.

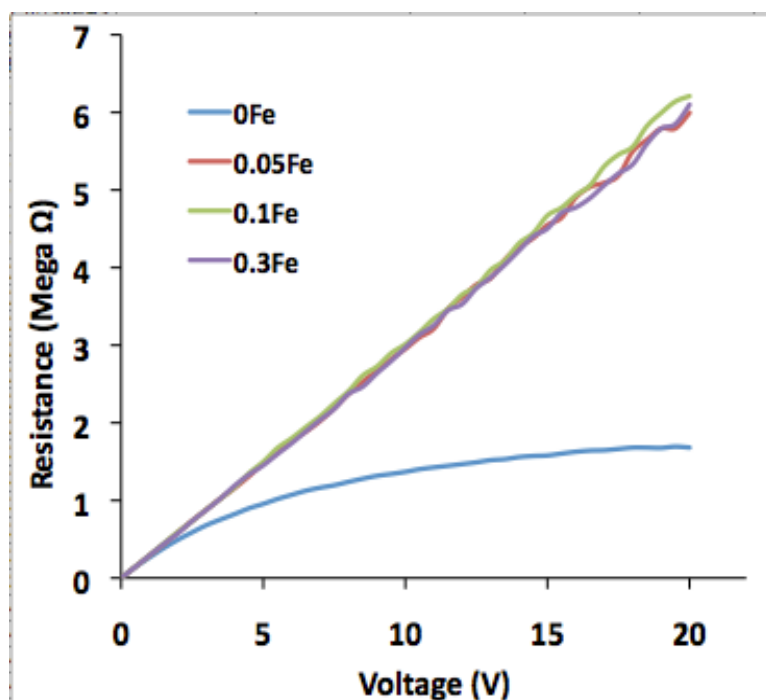


Figure 38. Resistance versus voltage for citrate gel synthesized mayenite $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$ samples with $x = 0, 0.05, 0.1$ and 0.3 .

Tables

Table 16. Refined lattice parameters for mayenite and phase fractions in $\text{Ca}_{12-x}\text{Fe}_x\text{Al}_{14}\text{O}_{33}$.

Sample	Lattice constant (Å)	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (Wt %)	CaAl_2O_4 (Wt %)	$\text{Ca}_2\text{Fe}_{0.7}\text{Al}_{1.3}\text{O}_5$ (Wt %)
$\text{Ca}_{11.9}\text{Fe}_{0.1}\text{Al}_{14}\text{O}_{33}$	11.9850(4)	93.7	6.3	0
$\text{Ca}_{11.8}\text{Fe}_{0.2}\text{Al}_{14}\text{O}_{33}$	11.9866(4)	89.5	10.5	0
$\text{Ca}_{11.7}\text{Fe}_{0.3}\text{Al}_{14}\text{O}_{33}$	11.9865(5)	74.0	19.0	7.0
$\text{Ca}_{11.6}\text{Fe}_{0.4}\text{Al}_{14}\text{O}_{33}$	11.9877(8)	63.2	21.7	15.2

Table 17. Phases identified using X-ray powder diffraction and refined wt% in $\text{Ca}_{12}\text{Al}_{14-x}\text{Fe}_x\text{O}_{33}$.

Synthesis Technique	Fe (x)	Phases Present (wt %)
Solid-State	0	C_{12}A_7
	0.1	C_{12}A_7 (99.7), C_3A (0.3)
	0.2	C_{12}A_7 (96.4), C_3A (3.6)
	0.5	C_{12}A_7 (95.9), C_3A (3.4), C_2AF (0.7)
	0.6	C_{12}A_7 (96.6), C_3A (<0.1), C_2AF (3.4)
Citrate Gel	0	C_{12}A_7
	0.05	C_{12}A_7
	0.1	C_{12}A_7
	0.2	C_{12}A_7
	0.3	C_{12}A_7
	0.4	C_{12}A_7 , C_5A_3 (less than 0.1)

CONCLUSION

Conclusions

Doped and undoped mayenite samples were successfully synthesized using both solid-state and citrate gel techniques. During firing, mayenite prepared using the citrate gel method reached equilibrium at 850 °C in about three hours, compared to solid-state synthesized samples, which requires a temperature of at least 1200 °C and about 16 hours to reach equilibrium. Measured viscosity on a gel prepared using the citrate gel synthesis was found to increase with increase in the shear stress applied.

The temperature calibrations were carried out on the platinum strip heater stage used in the high temperature x-ray diffraction measurements and confirmed that set points were higher than the temperature of sample surface. High temperature x-ray diffraction data collected on samples synthesized using the citrate gel technique in-situ in air at temperatures of 600 °C and below showed only amorphous content; however, data collected at higher temperatures indicated the first phase to crystallize is CaCO_3 and when fired in air at 800°C showed multiple phases including calcite. When fired ex-situ at 900 °C or above, x-ray powder diffraction data showed single-phase mayenite. In contrast high temperature x-ray diffraction data collected in 4% H_2 /96% N_2 does not show the presence of CaCO_3 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ starts to form around 850 °C, however, at higher temperatures the metastable phase $\text{Ca}_5\text{Al}_6\text{O}_9$ is produced. $\text{Ca}_5\text{Al}_6\text{O}_9$ is also observed when the amount of citric acid is reduced during the synthesis.

$\text{Ca}_5\text{Al}_6\text{O}_9$ is favored at higher temperatures and with less oxygen. DTA/TGA data support unique phase evolution paths for the two different environments. Particles produced by the citrate gel method show more and smaller pores compared to particles synthesized using the solid-state technique, however, BET surface area analysis shows that the citrate gel synthesis does not produce mayenite with high surface area.

Fe was introduced into mayenite and samples were synthesized both for replacement on Ca site and replacement on Al site using solid-state method, and for replacement on Al site using the citrate gel synthesis. Samples prepared using citrate gel were able to incorporate more Fe while maintaining phase purity while solid-state samples showed multiple phases. It was observed that beyond 0.4 atomic %, Fe started to precipitate out. Fe was found to replace Al instead of Ca in the framework, and the lattice parameter of mayenite was observed to increase with increased Fe content as a result of the larger ionic radius in Fe than the Al. There was a decrease in conduction from the undoped to the doped mayenite, suggesting that Fe is not an appropriate dopant in enhancing the electrical properties of mayenite.

Future Work/Recommendation

Since it is established that citrate gel synthesis allows the incorporation of impurities better than solid-state synthesis, vanadium doped mayenite should be

prepared using citrate gel method to see if phase purity can be achieved. The dopants were randomly chosen, it will be of interest to have some theoretical modeling and simulation as to predict which dopant would enhance the electrical properties in mayenite and at the same time not compromise the optical properties. The density function theory (DFT) will be a useful tool in doing this.

VITA

Sabina N. Ude was born in Enugu, Enugu State in Nigeria. She is married with children. Sabina obtained her Bachelors degree in Metallurgical and Materials Engineering in 2000 from Enugu State University of Science and Technology in Nigeria. Her Masters degree in Materials Science and Engineering was received from the University of Tennessee Knoxville in 2010. Sabina was a Pipeline Engineering Diversity Fellow from August 2008 to July 2010. In 2012 she became a Mickey Leland Energy Fellow, offered through the office of fossil energy, U.S. department of energy. She acquired her Ph.D degree in Materials Science and Engineering in 2013 from the University of Tennessee Knoxville. After twelve years in the United States, Sabina hopes to return to Nigeria and become a professor.