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Metastable Phases of MgO-TiO$_2$ Solid Solutions

Liang-Chieh Ma

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METASTABLE PHASES OF MgO-TiO$_2$ SOLID SOLUTIONS

by

Liang-Chieh Ma

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Construction Engineering, Materials Engineering,
and Industrial Design

Western Michigan University
Kalamazoo, Michigan
December 2002
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2002
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Liang-Chieh Ma
METASTABLE PHASES OF MgO-TiO₂ SOLID SOLUTIONS

Liang-Chieh Ma, M.S.

Western Michigan University, 2002

Magnesium titanium oxide powders were synthesized by the sol-gel method using alkoxides of magnesium and titanium with different ratios. Metastable phases of qandilite, Mg₂TiO₄, were found with Mg:Ti ratios down to 1.52:1 in lower temperature 600 °C than in the equilibrium condition which is above 1200 °C. Powder samples were examined by neutron powder diffraction and X-ray photoelectron spectroscopy (XPS) for analysis of structure and oxidation states. Also, samples were tested for the Mg:Ti ratios by induced coupled plasma atomic emission spectrometry. The structure refinements of the samples were done by General Structure Analysis System (GSAS) using the Rietveld refinement method. Particle sizes were calculated from structure refinement. For the X-ray photoelectron spectroscopy analysis the commercial geikielite, MgTiO₃, and qandilite, Mg₂TiO₄ which was annealed at 1180 °C were used as references when were compared with nanostructured samples. The XPS results showed that Ti cations had lower oxidation states in the metastable samples with Mg:Ti ratios 1.52:1 and 2:1 than in the sample that was created under the stable condition in order to keep charge balance for the samples.
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CHAPTER I

INTRODUCTION

Development of Nanostructured Materials

Nanomaterials can be traced back to more than millions of years ago in biological systems. For example, certain species of bacteria can orient themselves because they are able to make use of a chain containing nanoparticles of single-domain magnetite Fe$_3$O$_4$ (Edelstein & Cammarata, 1998).

However, the first scientific work in this field appeared in 1861 when British chemist Thomas Gresham created a colloid to describe a solution containing nanoparticles in a suspension (Edelstein & Cammarata, 1998). The first idea of "small size" and discussion about the advantage of controlling "size" is written by Feynman in his article "There is plenty of room at the bottom" (Feynman, 1992). The investigation of this field expanded over time, but changed dramatically when Professor Richard Smelly won the 1996 Nobel Prize for the discovery of C$_{60}$ (Nalwa, 2001). The idea of designing nano-sized products became popular. A variety of applications of "smart and small" materials and devices can be accomplished by controlling the manufacturing into a nanoscale.

Generally speaking, nanostructured material can be defined as a material having a particle diameter, grain size, layer thickness, or characteristic length (such as
the width of a line on matrix), which is less than about a hundred nanometer. The electronic, magnetic, optical, mechanical, and chemical properties of nanostructured materials differ from conventional materials arising from the difference of solid-state structures (Wang, 2000). The particle or crystalline size can have influence on many aspects such as on chemical bonding, delocalization of charges, surface area, and geometry. All of these can be considered a component of solid state structure. A lot is still unknown in this field from fundamental elements to solid states (Goldstein, 1997).

Nanostructured materials have plenty of superior properties to conventional micro and macro-grained materials. Some novel applications include carbon nanotube, mems, quantum devices and multilayer thin films, nanocrystals, and nanowire crystals (Klabunde, 2001).

Properties and Synthesis of Nanostructured Ceramic

Ceramic powders play an important role in the synthesis of ceramic materials. The particle size has significant influence on the properties of the final product. The science of ceramic nanoparticles has been investigated for many years with much success in several areas including synthesis, surface science, texturology, destructive absorption, catalysis, etc. (Klabunde, 2001). Compared with conventional ceramic powders, nanosize ceramic powders exhibit higher density and strength properties in the final product because they have lower percentage of vacancies and more grain boundaries.
The synthesis of nanoscale ceramic powder attracts more and more attention because of the potential for new materials and properties. Several synthesis methods have been reported, for example, gas condensation techniques, spray pyrolysis, and thermochemical decomposition (Klabunde, 2001). The sol-gel method is often used for ceramic oxide nanopowder and has many advantages over other methods. For example, the homogeneity of the product can be very high and the particle size can be very small. This process involves two essential steps: Hydrolysis and Condensation (Klabunde, 2001). These are the two most important steps to determine the properties of final product. Sol-gel starts with precursors mixed in nanosize scale, and it has respectively low processing temperatures and high control of the stoichiometry and high homogeneity that results in more desirable properties of nanomaterials (Goldstein, 1997).

Properties and Application of Magnesium Titanates

Magnesium titanates are important as industrial ceramics. They are often used as insulators because of their dielectric properties. Nanocrystalline magnesium titanates powders show high and stable dielectric constant over a wide range of both applied temperature and frequency thus they are ideal materials to make capacitors (Zabicky et al., 1997).
CHAPTER II

THEORETICAL BACKROND

Magnesium Titanates

MgO-TiO₂ Phase Diagram

Three intermediate compounds in the MgO-TiO₂ system are shown in Figure 1. Mg₂TiO₄ and MgTi₂O₅ are stable phases only at high temperature because of the entropy arising from cation disorder (Weschслer & Navrotsky, 1984).

Figure 1. Phase Diagram of MgO-TiO₂ System (Weschслer & Navrotsky, 1984).
Mg₂TiO₄, MgTiO₃ and MgTi₂O₅ are the minerals qandilite, geikielite and karrooite, respectively. Qandilite and geikielite were usually found to be stable only at high temperatures. At low temperature Qandilite is predicted unstable relative to a mixture of MgTiO₃ plus MgO and karrooite relative to a mixture of MgTiO₃ plus TiO₂. (Weschler & Navrotsky, 1984).

Descriptions of crystallization of MgO-TiO₂ phase diagram at high temperature are shown in Table 1 and Figure 2. The vertical lines intersecting the triple point or the specific compound composition in Figure 2 can simply divide the crystallization. Crystallization types and specifications are listed in Table 1.

Figure 2. Analysis of Crystallization Types of Binary MgO-TiO₂ (McHale, 1998).
Table 1

Description of the MgO-TiO$_2$ System above 1500°C (McHale, 1998)

<table>
<thead>
<tr>
<th>Region</th>
<th>Range (mol% TiO$_2$)</th>
<th>Liquidus [°C]</th>
<th>Primary phase</th>
<th>Solidus [°C]</th>
<th>Solid phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-33</td>
<td>≥1810</td>
<td>MgO</td>
<td>1760</td>
<td>MgO + Mg$_2$TiO$_4$</td>
</tr>
<tr>
<td>2</td>
<td>33-39</td>
<td>1810-1760</td>
<td>MgO</td>
<td>1660</td>
<td>Mg$_2$TiO$_4$ + MgTiO$_3$</td>
</tr>
<tr>
<td>3</td>
<td>39-50</td>
<td>1760-1700</td>
<td>Mg$_2$TiO$_4$</td>
<td>1660</td>
<td>Mg$_2$TiO$_4$ + MgTiO$_3$</td>
</tr>
<tr>
<td>4</td>
<td>50-53</td>
<td>1700-1660</td>
<td>Mg$_2$TiO$_4$</td>
<td>1660-1620</td>
<td>MgTiO$_3$s + Mg$_2$TiO$_5$</td>
</tr>
<tr>
<td>5</td>
<td>53-54</td>
<td>1660-1650</td>
<td>MgTiO$_3$</td>
<td>1620-1605</td>
<td>MgTiO$_3$s + Mg$_2$TiO$_5$</td>
</tr>
<tr>
<td>6</td>
<td>54-61</td>
<td>1650-1605</td>
<td>MgTiO$_3$</td>
<td>1605</td>
<td>MgTiO$_3$s + Mg$_2$TiO$_5$</td>
</tr>
<tr>
<td>7</td>
<td>61-67</td>
<td>1605-1660</td>
<td>Mg$_2$TiO$_5$</td>
<td>1605</td>
<td>Mg$_2$TiO$_5$ + MgTiO$_3$s</td>
</tr>
<tr>
<td>8</td>
<td>67-76</td>
<td>1660-1630</td>
<td>Mg$_2$TiO$_5$</td>
<td>1630</td>
<td>Mg$_2$TiO$_5$ + TiO$_2$</td>
</tr>
<tr>
<td>9</td>
<td>76-100</td>
<td>1630-1815</td>
<td>TiO$_2$</td>
<td>1630</td>
<td>Mg$_2$TiO$_5$ + TiO$_2$</td>
</tr>
</tbody>
</table>
Qandilite (Mg₂TiO₄)

Qandilite, Mg₂TiO₄, has the inverse spinel structure A₂BX₄ with space group fdl₃m. Spinel structure is characterized as a cubic, closed-packed array of O⁻² spheres. However, the Mg₂TiO₄ undergoes a cubic-tetragonal transition at about 933K (Wechsler & Von Dree, 1984).

The spinel structure B₂AO₄ is cubic with a unit cell containing 32 oxygen ions with 16 A²⁺ cation in 32 octahedral interstitial positions and 8 B³⁺ cations in 64 tetrahedral interstitial positions (Richerson, 1992). Thus, the occupancy of octahedral and tetrahedral positions are 1/8 and 1/2.

To describe the inverse spinel structure shown in Figure 3, the formula of a spinel structure maybe written \((A_{(1-X)}B_X)_{\text{tet}}[A_XB_{(2-X)}]_{\text{oct}}O_4\) where X is called inverse parameter. If X=0, normal spinel structure results \(A_{\text{tet}}B_2_{\text{oct}}O_4\). If X=1, completely inverse spinel structure have formula \(B_{\text{tet}}(AB)_{\text{oct}}O_4\) (O’Neill et al, 1997). In the case of Mg₂TiO₄, the formula may be written as \([\text{Mg}^{2+}]_{\text{tet}}[\text{Mg}^{2+}\text{Ti}^{4+}]_{\text{oct}}O_4\) where 50% Mg²⁺ occupy 1/8 tetrahedral site and another 50% Mg²⁺ accompany Ti⁴⁺ to occupy 1/2 octahedral site (O’Neill et al, 1997). An inverse spinel structure of qandilite is shown in Figure 4.
Figure 3. The Inverse Spinel Structure of Qandilite (Von Hippel, 1954).

Figure 4. A Inverse Spinel Structure of Qandilite.
**MgTiO$_3$**

MgTiO$_3$, geikielite, has the ilmenite structure with space group $R3$ (Wechsler & Von Dreele, 1989). Ilmenite structure is derived from the corundum structure by ordering the cations into two nonequivalent octahedral sites (Richerson, 1992). In geikielite, Mg$^{2+}$ and Ti$^{4+}$ cations fit the octahedral sites alternatively layer by layer along the hexagonal $c$ direction which is shown Figure 5 (Chiang, 1997). A ilmenite structure of geikielite is shown in Figure 6.

![Figure 5. Structure of Geikielite, Showing Only the Cation Sublattice (Chiang et al., 1997).](image-url)
Figure 6. An Ilmenite Structure of Geikielite.
Synthesis of Ceramic Nanoparticles

The powder process plays an important role in the processing of ceramic materials. Particle size distribution, shape, structural properties (crystalline or amorphous structural morphology), and chemical properties (composition, interface, and surface area) have a significant influence on ceramic material processes such as sintering and densification and on the properties of the final product (Richerson, 1992).

Synthesis of ceramic nanopowders can be achieved by several methods. These methods can be classified into physical aerosol methods and chemical routes. Physical aerosol methods include the vapor condensation method, spray pyrolysis, and thermal chemical decomposition. Chemical routes include the sol-gel technique, reverse microemulsions method, low temperature wet-chemical synthesis, chemical synthesis of preceramic polymers coupled with physical processing techniques, and mechanochemical synthesis method (Klabunde, 2001). Each method has its own strength; thus, selection of the synthesis method depends on the required properties of powders such as particle size, size distribution, particle agglomeration, chemical homogeneity, and purity.

Several synthesis methods have been reported for magnesium titanates powders. Conventional solid-state reaction (Wechsler, 1984) forms magnesium
titanates powders by calcination of MgO and TiO$_2$ powders in stoichiometric proportions. Calcination refers to a high-temperature treatment to modify the characteristics of powders (Richerson, 1992). However, calcinations and grinding processes usually result in undesirable grain growth and contamination. Precipitation methods involve Mg and Ti hydroxides coprecipitates at a very high pH value around 10-12 (Abothu et al., 1999). This method requires such a high pH value to ensure complete precipitation, so it is not easy as other method for the preparation and controlling.

Thermal chemical decomposition requires a very high temperature to synthesize a compound from peroxide precursors (Klabunde, 2001), so it consumes energy and time to reach the require temperature. The most recently synthesized methods are the mechanochemical method (Zabicky et al., 1999) and nanocomposite and the monophasic method. The former one involves the milling of precursors to form a nano-scale composite. After heating, the reaction of the nano-scale composite forms desirable particles within a matrix that is a by-product in this reaction. By removing the matrix, nano-scale particles are obtained (Klabunde, 2001).

**Sol-Gel Method for Metal Oxides**

The process used to prepare metal oxides by sol-gel is usually the hydrolysis of reactive nanometer precursors (Bengisu, 2001). Alkoxides, which can be written in the general formula M(OR)$_n$, are usually used as the precursors where M is a metal ion and R is an alkyl group. A typical sol consists of alkoxides in an alcoholic solution.
Hydrolysis of metal alkoxides results in corresponding hydroxides in the sol. The reaction can be expressed as follows:

The hydrolysis reaction: \( M(OR)_n + n \text{H}_2\text{O} \leftrightarrow M(\text{OH})_n + n \text{ROH} \)

Hydrolysis is followed by condensation to form \( M\text{--O--M} \) bonds by either one of two reactions (Zelinski & Uhlmann, 1984):

(a) Dehydration:

\[
\text{--M--OH} + \text{HO-M} \rightarrow \text{--M--O--M--} + \text{H}_2\text{O}
\]

(b) Dealcoholation:

\[
\text{--M--OH} + \text{RO-M} \rightarrow \text{--M--O--M--} + \text{ROH}
\]

Condensation of the hydroxide molecules that is achieved by dehydration or dealcoholation leads to the formation of a network of metal hydroxide.

When all hydroxides are linked in one network-like structure and the molecular structures are no longer reversible, a "gel" is formed. This point is known as a sol-gel transition point (Goldstein, 1997). Gel is a polymer of a three dimensional skeleton involving inter and intra pores. Removal of the solvents in gel results in ultra fine powders of the metal hydroxides. By calcination of the gel, the hydroxides transform to oxides and ultra fine metal oxide powders are obtained.

Calcination under different conditions results in different types of gel. Under normal condition, gel network shrinks because of capillary pressure, and the
hydroxide product is referred as xerogel (Klabunde, 2001). Nevertheless, under high pressure at a temperature higher than the critical temperature of the solvent, less shrinkage of the gel network results in aerogel (Klabunde, 2001).

Sol-gel processes have several advantages for the synthesis of nano-sized metal-oxide powders. For example, homogeneity of the product can be very high because the homogenous mixing of the starting materials can be achieved at the molecular level. In addition, the particle size can be very small because the process starts with a nano-sized unite. Sol-gel method controlled the particle size, morphology, and surface chemistry at the same time (Edelstein & Cammarata, 1998).

Synthesis of magnesium titanates by the sol-gel method can be achieved from the alkoxide of magnesium and the alkoxide of titanate. A stoichiometric mixture of the hydroxides of magnesium and titanium can be precipitated from alcoholic or non-hydroxylic solvents. Dehydration occurs at a relatively low temperature (595 °C) to eliminate hydroxide group to obtain nanoparticles of magnesium titania (Zabicky et al, 1997).

Diffraction Technique

**Neutron Diffraction**

Since the recognition of the wave nature of neutrons in 1936, neutron diffraction has become a very powerful technique in studying crystallography especially for nanostructured materials (Brundle, 1992).
Like X-ray and electron diffraction, neutron diffraction has the capability to characterize crystalline materials for their structures. The basic concepts for both X-ray and neutron diffraction are based on Bragg's law. The intensity of the Bragg's peak is strongly dependent on the nature and the numbers of atoms lying on the specific crystal plane.

An important difference between neutron and X-ray diffraction is the scattering matter, which scatters the neutrons from these two kinds of waves. Neutron beam is scattered by the nuclei rather than outer electrons that scatter the X-ray beam. Therefore, neutron diffraction reveals the distributions of the matter while X-ray reflects the electron density of a solid (Brundle, 1992). In neutron diffraction, the scattering intensity varies erratically as atomic weight increases as shown in Figure 7 (Bacon, 1954). This arises from the superposition of resonance on a slowly increasing potential scattering. The resonance of scattering nuclei causes the irregular changes in reactive area of the scattering nuclei with increased atomic weight. Figure 8 compares the reactive areas which indicate the intensity in neutron and X-ray diffraction.
In X-ray scattering, the intensity increases as a function of atomic number because the bigger electron cloud increases the possibility of scattering. As shown in Figure 7, with increasing scattering angle, the X-ray’s intensity drops dramatically.
with even the same atomic weight.

The second difference lies in the penetration depth of between X-ray and neutron diffraction. This is because of the absorption of X-ray when a beam of X-ray interacts with samples. Generally, X-ray diffraction analysis can have a sample with thickness to 10 µm while neutron diffraction can have a penetration depth much deeper than 50 µm. (Brundle et al., 1992)

Furthermore, neutron diffraction has better sensitivity to the magnetic structure. The magnetic moments of neutrons interact with the magnetic moments of the target atoms. When magnetic moments of neutrons interact with the moments of the target atoms, the interaction is much stronger than for X-rays (Brundle et al., 1992).

Neutron Source

Steady-state methods and pulsed neutron source are two main methods for neutron diffraction (Brundle et al., 1992). Steady-state method is a conventional neutron source to provide neutrons. It provides continuous flux and wavelengths of neutrons from the nuclear fission in an nuclear reactor. For a diffraction analysis, a narrow band of neutron wavelength is selected by a monochromator. By varying the diffracting angle θ, d spacing values of a sample can be scanned by diffraction peak.

Because the development of accelerator technology, intense pulsed neutron sources are available (Jorgensen et al., 1989). Different from steady-stated method, the neutrons come from the process called “spallation”. This process utilizes fast
charged particles, such as high-energy protons, accelerated by a high-energy accelerator to bombard a heavy atomic nucleus (for example, Uranium target). Some neutrons "spalled" or knocked from the target to generate a pulsed neutron source with a frequency of 30-120 pulses per second having continuous wavelengths (Brundle et al., 1992). For a diffraction analysis, pulsed sources use almost the entirely available neutron spectrum, fix the scattering angle and simultaneously detect a neutron while determining its time of flight (see page 19). A comparison of steady-state method and pulsed neutron source is shown in Figure 9.

Figure 9. Comparison of Steady-State and Time of Flight Method (Brundle et al.,
For many research problems of a crystal structure, having neutrons in a series or pulse are better than having a continuous neutron source. First, neutron pulses can be produced with a much higher intensity than that available from continuous sources. Second, each pulse contains neutrons of a range of wavelengths and energies. This enables the "time of flight" method to collect data from each source pulse. Furthermore, unlike the conventional continuous neutron source, it is not necessary to move around the sample during experiment, making it easy to arrange a larger detector array or multidetectors around the sample (Anonymous, 2002).

**Time of Flight Method of Neutron Powder Diffraction**

The pulsed neutron source allows the “time of flight” (TOF) diffractometers to achieve high resolution by using a long incident flight path. Neutrons with different energies and wavelengths in the incident beam are scattered by the samples. Because different energy neutrons have different velocities, the time of neutrons traveling from the source to the detector are different. TOF method measures the time of flight of a neutron in a fixed length L from the source to the detector. Then neutron wavelengths are measurable with momentum according to the de Broglie equation (Jorgensen et al., 1989).

\[ \lambda = \frac{h}{m \nu} = \frac{t}{mL} \]
where $\lambda$ is neutron wavelength, $h$ is Planck’s constant, $m$ is neutron mass, $V$ is neutron velocity, and $t$ is the measured TOF.

The Rietveld Refinement Method for Neutron Powder Diffraction

**Introduction**

This refinement method is named “Rietveld” after the person who was the first one to develop a computer-based analytical procedure and freely shared it in public at 1967 (Young, 1993). The main purpose of this method is to calculate structure parameters (i.e. lattice parameter, atom coordinates and thermal parameters) and profile parameters (i.e. U, V, W and diffractometer zero point) from diffraction patterns (Von Dreele et al, 1982).

Rietveld refinement has been applied to both X-ray and neutron powder diffraction very successfully.

**Basic Principle**

A powder diffraction pattern may be thought as a collection of individual reflection profiles, each of which has a peak height, peak position, breadth, tail and an integrated area which is proportional to the Bragg intensity (Young, 1993). It tends to be a Gaussian distribution with a full-width at half-maximum (FWHM) as a function of diffraction angle $\theta$:

$$(\text{FWHM})^2 = U \tan^2 \theta + V \tan \theta + W$$

(1)
where $U$, $V$, and $W$ are the refineable profile parameters (Young, 1993; Giacovazzo, 1992). The basic concept of the Rietveld method is to refine the calculated model (peak shape function) by minimizing the residual between the observed diffraction pattern and the calculated model in a least-square process:

$$S = \sum W_i | Y_{io} - Y_{ic} |^2$$

(2)

Where $W_i$, given by $(W_i)^{-1} = \sigma_i^2 = \sigma_{ip}^2 + \sigma_{ib}^{-2}$ is a suitable weight, $\sigma_{ip}$ is a standard deviation associated with the peak and $\sigma_{ib}$ is that associated with the background intensity $Y_{ib}$. $Y_{io}$ is the observed intensity at $i$th step and $Y_{ic}$ is the corresponding intensity calculated via the model (Giacovazzo, 1992). By adjusting the structure parameters and profile parameters, the least-square fit is obtained; then, the structure and profile parameters, which make the best fit for all profiles, are determined.

The Rietveld method constructs a calculated model as expressed below:

$$M ( S_i, X) = b (S_i, X_b) + \sum_{k=k_1}^{k_2} I_k (X_s) \phi (S_rS_k, X_p)$$

(3)

where $M$ is the model that predicts a set of intensities and $X_b$, $X_s$ and $X_p$ are, respectively, background, structure, and peak shape parameters and $S_i = 2\sin \theta_i / \lambda_i$. The term $b (S_i, X_b)$ is a background function, $I_k (X_s)$ is the integrated intensity of the Kth Bragg function, $\phi (S_rS_k, X_p)$ is a peak shape function (profile function) normalized so that the sum over the whole range of the peak is 1, and the sum is over all reflections that can contribute to the intensity at $S_i$ (Young, 1993).
Determination of Particle Size

The term “particle size” is usually used as the same meaning of “crystallite size” if the individual crystal size is less than 0.1 µm (Cullity, 1990). Determination of particle size is achieved by the broadening of the diffraction peak.

\[ P = \frac{C K}{\gamma^2} \]  \hspace{1cm} (4)

Where C is the diffractometer constant, K is the Scherrer constant, and \( \gamma^2 \) is one of the profile coefficients (Larson and Von Dreele, 1985-).

Refinement Procedures

In the beginning of the refinement, one must have the correct space group, fairly close lattice parameter, and atom coordinates. Also, one needs the initial estimated values of U, V, and W. Before the refinement of structural or profile parameters can be started, the positions of the observed and calculated peaks must match well (McCusker et al, 1998).

In the article “Introduction to the Rietveld method” Young suggests that there is a suggested parameter turn-on sequence to avoid false refinement. The structure should be refined to ease convergence and to avoid divergence. The correlation of parameters—for example, the occupancy parameter and the thermal parameters are highly correlated with each other (McCusker et al., 1998)—may cause the divergence of refinement. To avoid this situation, Young suggests that in the beginning of refinement, it is better to refine only few parameters at the same time.
Auger and X-Ray Photoelectron Spectroscopy

Introduction

The photoelectric process, discovered in the early 1900s, was developed for analytical use in the 1960s, largely due to the work of Kai Siegbahn’s group (Brundle et al., 1992).

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are important techniques for the surface characterization of materials. Because of the surface sensitivity, XPS has become a very broadly applicable surface analysis technique. It can collect the information from a depth of ~10 nm under the sample surface to provide a quantitative and chemical state analysis (Brundle et al., 1992). Except hydrogen and helium, AES and XPS can detect all elements except hydrogen and helium in the periodic table with a sensitivity variation around 30 (Brundle et al., 1992). The application can be applied to materials like biological, organic, and polymeric materials all the way to metals, ceramics, and semiconductors.

Auger electrons and X-ray photoelectrons are usually generated at the same time during the photoionization process. For an XPS analysis, Auger peaks can provide additional chemical state identification because sometimes it is impossible to directly distinguish a certain chemical state from the XPS core level. Compared with these two sources, AES provides more elemental information while XPS provides more chemical information. In surface analysis, each of them has its own strength, most of the time they are complementary (Brundle et al., 1992).
Basic Principles of XPS

A photon with sufficient energy (short enough wavelength) can ionize an atom, producing photoelectrons ejected as free electrons. The kinetic energy (KE) of the photoelectron depends on the energy of the photon $hv$ expressed by Einstein photoelectric low:

$$KE = hv - BE$$

(5)

where $BE$ is the bonding energy of the particular electron concerned. KE can be detected from a known $hv$ photon, thus, the BE can be determined. Since BE is the energy required to remove the specific electron from the atom, it is strongly dependent on the types of nuclei and the chemical states in which electrons bonded. If we assume all the other electrons did not respond or interact in the same way, BE is approximately equal to the eigenvalue $\epsilon$ of an atom in a specific bonding. Thereby, from the KE of the ejected photoelectron, the atom with a specific chemical state can be identified.

Photoelectron Process and Spectrum

A monochromatic soft X-ray, is usually used to photo-emit electrons from core levels of elements in XPS (Brundle et al., 1992).

Consider a carbon atom as an example shown in Figure 10 (a). It has six electrons, two each in the $1s$, $2s$, and $2p$ orbitals, written as C $1s^22s^22p^2$. The photoelectron process occurs when a photon transfers its energy to an electron in the
$1s$ level and the photoelectron is emitted from the $1s$ level with a KE$_{1s}$ as shown in Figure 10 (a). Alternatively, for any individual C atom, a $2s$ or $2p$ electron might be emitted, too. During the photoelectron emission process, all three groups of electrons will be emitted so three different KE will be detected. Then the number of emitted photoelectrons vs. KE can be plotted. This is the photoelectron spectrum and is shown in Figure 10 (b).

In Figure 10 (b), the intensity of C $1s$, C $2s$, and C $2p$ are different because the probability for photoelectron emission from each orbital (photoionzation cross section, $\sigma$) is different. The cross section also varies with different atoms even for the same orbital.

The numbers of peaks in the spectrum indicates the numbers of occupied energy levels in the atoms whose BE are lower than $h\nu$. The location of the peaks (specific BE for each orbital) identifies the atom concerned because each element atom has its own characteristic BE. All the statements above are based on the assumption that all electrons behave independently.
After the photoemission process is over, there might be an Auger electron emitted too. In Figure 10 (c), a hole left because of the emitted $1s$ electron, can be eventually filled by an electron from a higher energy level. The energy released during relaxation may be sufficient to eject another electron from the same level. This second ejected electron is called Auger electron. The KE of an Auger electron can be calculated from:
KE (Auger) = (ε_{1s}-ε_{2p}) - ε_{2p} \tag{6}

Elemental and Chemical State Analysis

The energy levels can be divided into two types: core level and valence level. Core level is the energy level of the electrons in the inner shell of atoms. For example, in Figure 10(a), C 1s is the core level. Because it is not involved in the process of chemical bonding with other atoms, it is nearly a constant (within a few eV deviations) from different chemical bonding of the concerned atoms. So, the BE of core level will be independent on the chemical bonding of atoms and gives each element atom a fingerprint (Brundle et al., 1992). Quantitative analysis, which yields relative atomic concentrations, can be achieved by measuring the relative peak intensities of core level BE because the relative peak intensities are proportional to the numbers of atoms.

For chemical analysis, we need to consider the variation of the core level BE for the same atom in different chemical environment. Different bonding results in a shift of several eV of the peak on the spectrum as shown in Figure 11. This is called chemical shift, ΔBE (Brundle et al., 1992). It has a trend to higher positive charge with higher BE. In Table 3, different chemical states that result in different chemical shifts are given for example. However, not all atoms can be distinguished by chemical shift; for example, Cu\(^0\) has the same chemical shift as Cu\(^+\) within the instrument precision. Therefore, we need to consider not only chemical shift but also other features on spectrum for complete chemical analysis.
<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation State</th>
<th>Chemical shift from zero-valent state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni$^{2+}$</td>
<td>-2.2 eV</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe$^{2+}$</td>
<td>-3.0 eV</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>-4.1 eV</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti$^{4+}$</td>
<td>-6.0 eV</td>
</tr>
<tr>
<td>Si</td>
<td>Si$^{4+}$</td>
<td>-4.0 eV</td>
</tr>
<tr>
<td>Al</td>
<td>Al$^{3+}$</td>
<td>-2.0 eV</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu$^{+}$</td>
<td>-0.0 eV</td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>-1.5 eV</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn$^{2+}$</td>
<td>-0 eV</td>
</tr>
<tr>
<td>W</td>
<td>W$^{4+}$</td>
<td>2 eV</td>
</tr>
<tr>
<td></td>
<td>W$^{6+}$</td>
<td>4 eV</td>
</tr>
</tbody>
</table>
In reality, the electrons do not behave independently. When a hole is created in a core level, other electrons will move toward the hole and have a relaxation. This is called “final state effects.” There is also a probability that a valence electron will be excited during the relaxation process, called “shake up” process shown in Figure 12. An Auger electron may be ejected, too. Considering all these spectral features can help and complete more accurate chemical analysis.
Figure 12. Shake up Structure (a). A core-level photoelectron ejection process (b). Core-level photoelectron ejection process with shake-up (c). Schematic XPS spectrum from (a) plus (b). (d). Cu $2p_{3/2}$ XPS spectrum for Cu$^+$ in Cu$_2$O and Cu$^{2+}$ in CuO. The latter shows strong shake-up features (Brundle et al., 1992).

Surface Sensitivity

A photoelectron generated during the photoelectric process has a limited length from the depth of sample d to the sample surface. There is an inelastic electron scattering before a photoelectron can leave the sample surface. Therefore, the detected intensities (flux of electrons) have a relationship with the original intensity under the
depth \( d \) according to the equation (Brundle et al., 1992):

\[
I_d = \frac{-d}{I_0 \lambda_e \sin \theta}
\]  

(7)

Where \( \theta \) is the angle of electron emission, \( d \)-depth and \( d / \sin \theta \) is the distance traveled through the sample at that angle \( \theta \). The quantity \( \lambda_e \) is called the “inelastic mean free path length”. \( I_0 \) is the flux of electron emission originating at depth \( d \) and \( I_d \) is the flux emerging without being scattered. The value of \( \lambda_e \), which determines quantitatively exactly how surface sensitive the measurement is, depends on the KE of the electron and the material through which it travels.

**Instrumentation**

A schematic XPS spectrometer is shown in Figure 13. The X-ray source is usually either Al K\( \alpha \) 1486.6 eV or Mg K\( \alpha \) 1253.6 eV radiation (Brundle et al., 1992). The spot size of the X-ray beam can be improved either by focusing the electron beam on the source target (anode) or by passing the X-ray through a monochromator. Reducing the spot size can improve the resolution of spectra.

Photoelectrons generated from the sample go through an electron lens before entering the energy analyzer. The electron lens slows the electrons in order to improve the energy resolution in the analyzer. It is also used to define an analyzed area on the sample.

The popular analyzer is a hemispherical sector with an applied voltage on the two hemispheres. By varying the voltage applied on the lens and analyzer, electrons
ejected from the sample with different KE are separated with different trajectories in the analyzer.

Pulse counting devices receive and count the electron flux of each pulse from analyzer. Then finally a XPS can be plotted by a computer receiving KE from analyzer and intensities from counting devices.

The spectrometers must operate under ultrahigh-vacuum pressure less than $10^{-9}$ Torr (Brundle et al., 1992). This is because samples contaminate rapidly under poor vacuum and electrons scattering in the air change KE significantly.

Figure 13. Schematic XPS spectrometer (Brundle et al., 1992).
Inductively Coupled Plasma Atomic Emission Spectroscopy

Inductively coupled plasma atomic emission spectroscopy, ICP-AES, is a powerful technology for multi-element analysis. The advantage of ICP-AES is its capability to simultaneously analyze up to 60 elements at one time. In addition, detection limits is very low in the range of 1-10 ppb. The inductively coupled plasma (ICP) is a high temperature source used for generating atomic vapor from an aqueous sample in an ICP-AES analysis. The plasma will reach a temperature in the range of 6,000 - 10,000° C, which will efficiently atomize most elements. A typical plasma source is shown in Figure 14. The green arrow represents the argon flow, and the blue arrow indicates the sample flow (Moore, 1989).

![Figure 14. A Typical Plasma Source (Moore, 1989).](image)

The basic concept of ICP-AES is to excite a sample into its constituent atoms and ions and cause them to emit light at a characteristic wavelength by exciting them to a higher
energy level. The elemental composition of the sample can be determined by observing the atomic and ionic emission lines emitted by the sample atoms in the high temperature plasma. A monochromator can separate specific wavelengths of interest, and a detector is used to measures the intensity of the emitted light. This information can be used to calculate the concentration of that particular element in the sample. This basic concept is illustrated in Figure 15.

Figure 15. Illustration of Basic Concept of ICP-AES (Moor, GL, 1989).
CHAPTER III

EXPERIMENT

Synthesis and Preparation of Powder Samples

Powder samples 91-74-2, 91-74-3, 91-75-1 were prepared by Professor J. Zabicky and co-worker at Ben-Gurion University of the Negev, Israel. The synthesis of powder samples was carried out by the sol-gel method (Zabicky et al., 1993). The precursors of ceramic oxide powders were precipitated from solution in anhydrous alcohol or non-hydroxylic solvents by hydrolysis of metal alkoxides with superheated steam at temperature 600 °C.

The general process is described by the reaction (1), where M represents a metallic element and R an alkyl radical (Zabicky et al., 1993). The precursor powders were synthesized after dehydration steps. In order to eliminate all the residual hydroxyl groups, the xerogels were calcinated at 600 °C. The final Mg:Ti ratios of the samples were related to the mixture of metal alkoxides and are obtained from the chemical analysis listed in the Table 3.

\[ \text{M(OR)}_n + n \text{H}_2\text{O} \rightarrow \text{M(OH)}_n + n \text{ROH} \] (1)
Table 3
Mg:Ti Atomic Ratios of Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg:Ti Atomic Ratio</th>
<th>TiO₂ Composition [mol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>91-75-1</td>
<td>0.9:1</td>
<td>52.6</td>
</tr>
<tr>
<td>91-74-3</td>
<td>1.5:1</td>
<td>40</td>
</tr>
<tr>
<td>91-74-2</td>
<td>2:1</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Commercial magnesium-titanium oxide (MgTiO₃ are purchased from Alfa Aesar company (99% purity, 2 µm powder). This was used for a standard sample for the XPS comparing with other samples.

Sample 91-74-2 1180 was made by heating part of 91-74-2 600 1180 °C for 3 hours and quenching in air. This sample was marked 91-74-2 1180 in order to distinguish it from 91-74-2 600.

Instruments and Analytical Procedures

Neutron Powder Diffraction

Neutron powder diffraction was performed at Arogonne National Laboratory. The neutron source is from Intense Pulsed Neutron Source (IPNS), and the diffractometer was General Purpose Powder Diffractometer (GPPD). The neutron beam came from the target uranium U-238. A schematic overall layout of GPPD is shown in Figure 16.
Figure 16. Schematic Diagram Showing the Overall Layout of GPPD (Jorgensen et al., 1989).

The wavelength is in the range of 0.02~0.57Å with beam size 12.7 mm wide. The detectors that were arranged around the diffractometer have different resolutions with different angles shown in Table 4.

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>Resolution $(\Delta d/d)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm 148^\circ$</td>
<td>$2.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\pm 90^\circ$</td>
<td>$4.9 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\pm 60^\circ$</td>
<td>$7.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Well characterized peak profiles and good resolution $\Delta d/d = 2.5 \times 10^{-3}$ at $2\theta = 148^\circ$ provide sensitivity to the presence of minority phases (Jorgensen et al., 1989).

The neutron diffraction is selected for our diffraction method because of its ability to distinguish the Ti and Mg. X-ray diffraction will have low resolution for Ti and Mg because their atomic weight are close with each other as shown in Figure 7. However, the neutrons have good resolution for them by the positive and negative scattering intensity also as shown in Figure 7.

**Diffraction Profile Analysis**

The data from GPPD were refined by the General Structure Analysis System (GSAS) software (Larson & Von Dreele, 1985-1994). The initial values of unit cell parameters, atomic positions and atomic fractions for three nanocrystalline phases, qandilite, geikielite, and karrooite were taken from Wechsler and Von Dreele (1989). The final refinement results from GSAS are listed and discussed in Chapter IV.

**Determination of Particle Size**

In equation (4), the diffractometer constant $C$ was 10385.98. A value of 0.1 was used for Scherrer constant $K$ (Langford & Wilson, 1978). $\gamma_2$ values were obtained from the refinement results of GPPD data. The unit of $P$ is nm.
X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) experiments were done by the chemistry department at Michigan State University. Samples 91-74-2 600, 91-74-2 1180, 91-74-3, 91-75-1, and commercial MgTiO$_3$ were analyzed by XPS experiment in order to obtain oxidation state value for magnesium, titanium, and oxygen ions.

The instrument used for XPS at Michigan State University is PHI 5000. Al Kα (1486.6 eV) was used as X-ray source. The experiment conditions are described in Table 5 and Table 6. All samples were scanned for spectra of Mg 2s, 2p, Ti 2p, and O 1s levels. C 1s level was also examined as an internal reference to eliminate the external charges. The binding energy for all the spectra should be calibrated by the external energy for each sample.

Table 5

Conditions for X-ray

<table>
<thead>
<tr>
<th>X-ray source</th>
<th>Al Kα (1486.6 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work function</td>
<td>4.8 eV</td>
</tr>
<tr>
<td>Pass energy</td>
<td>44.75 eV</td>
</tr>
<tr>
<td>Operation power</td>
<td>300 W</td>
</tr>
</tbody>
</table>

Table 6

Instrument Set Up

<table>
<thead>
<tr>
<th>Step size/eV</th>
<th>0.1 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time/step</td>
<td>21 sec.</td>
</tr>
<tr>
<td>Scan cycles</td>
<td>20</td>
</tr>
<tr>
<td>Pressure</td>
<td>$2 \times 10^{-8}$ Torr</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Temp</td>
<td>Around room temperature</td>
</tr>
</tbody>
</table>

The external charges would come from the instrument during the experiment and will be calculated by the measuring deviations from the binding energy of C 1s in each sample to the standard C 1s (285 eV) in general XPS analysis. The external charges will make the whole spectrum shift together with the same $\Delta BE$ and is not consistent in different samples. So, all line positions should be calibrated by this deviation to eliminate this charge effect.

The conductive carbon tape was used to hold the powder sample. The carbon inside the tape should be graphite. Calibration of the tape was well established by the experience of prior experiments.

**Inductively Coupled Plasma Atomic Emission Spectroscopy**

Inductively coupled plasma atomic emission spectroscopy, ICP-AES, was used for chemical analysis of sample composition at the Analytical Chemistry Laboratory at Argonne National Laboratory. The instrument is Perkin Elmer Optima 3300 ICP-AES system.

First, 50 mg of each sample were prepared as a solution with 5ml water, 3ml HCl and 250 $\mu$L HF into a Parr Bomb, a 23-ml Teflon digestion vessel (cup). Then the sealed Parr Bomb was placed in an oven at 140 °C overnight. After cooling next
morning, the Parr Bomb was opened and the contents quantitatively transferred to a 50 mL polyethylene volumetric flask. The materials were completely dissolved, so the solution was diluted to 50 mL with water and tested by the ICP-AES system.

An accuracy of 5% is attained for this analysis.
CHAPTER IV

RESULTS AND DISCUSSIONS

Chemical Analysis

The ratios of Mg:Ti that were tested by inducted coupled plasma atomic emissions spectrometry (ICP-AES) are listed in Table 7.

Table 7
Chemical Analysis Determination of Mg:Ti ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg:Ti [Wt %]</th>
<th>Mg:Ti:O [mol %]</th>
<th>Mg:Ti Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgTiO₃</td>
<td>17.9:38.2</td>
<td>20.0:21.7:58.2</td>
<td>0.9:1</td>
</tr>
<tr>
<td>91-75-1</td>
<td>17.5:37.2</td>
<td>16.4:17.7:66.0</td>
<td>0.9:1</td>
</tr>
<tr>
<td>91-74-3</td>
<td>22.7:29.2</td>
<td>20.5:13.4:66.1</td>
<td>1.5:1</td>
</tr>
<tr>
<td>91-74-2 600</td>
<td>25.7:25.5</td>
<td>22.8:11.5:65.7</td>
<td>2:1</td>
</tr>
</tbody>
</table>

The accuracy attained from this ICP-AES analysis is 5%. Only the weight percentage of Mg and Ti were tested. The oxygen weight percent is calculated by assuming that no other elements are present. So that all data listed in the columns Mg:Ti:O mol % and Mg:Ti atomic ratios are based on this assumption.

The Mg:Ti:O ratio of sample MgTiO₃ which is commercial geikielite was very close to 1:1:3. It conformed to the ratio of stoichiometric geikielite that is 1:1:3. This sample can be treated as a reference sample that gives the confidence to other results. Samples 91-75-1, 91-74-3 and 91-74-2 were obtained with Mg:Ti:O ratios that are all
non stoichiometric. The mass losses of samples 91-75-1 and MgTiO₃ during the heating before chemical analysis were also recorded in Table 8. The mass loss may have come from the absorbed moisture loss at 105 °C and the water from hydroxide and CO₂ from carbonates at 1000 °C for 2 hours. Although the mass loss is a small fraction of the samples mass, it still suggests that some “bound” water is present.

Table 8
Mass Loss from Chemical Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loss after 105 °C [Wt %]</th>
<th>Loss after 1000 °C [Wt %]</th>
<th>Total mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgTiO₃</td>
<td>0.013</td>
<td>0.324</td>
<td>0.34</td>
</tr>
<tr>
<td>91-75-1</td>
<td>0.35</td>
<td>1.25</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Mass loss shown in Table 8 indicates that there was water and other OH⁻ groups bonded to sample 91-75-1 versus commercial MgTiO₃. This is because the weight percentages which are detected after 105 °C and 1000 °C and the total mass loss percentage are much more significant in the sample 91-75-1. There is also mass loss in sample MgTiO₃ but much less than that in sample 91-75-1. The water or OH⁻ groups will not be inside the structure and may come from the residual hydroxyl groups that were not completely eliminated at the stage of calcination at 600 °C in the sol-gel process.
The profiles of diffraction patterns from neutron powder diffraction were refined by the Rietveld refinement method. The experimental and calculated profiles are attached in Appendix A. Phase analysis results from GSAS are presented in Table 9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg:Ti Atomic Ratio</th>
<th>TiO$_2$ in The Original Sol-gel Process [mol%]</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>91-74-2 1180</td>
<td>2:1</td>
<td>33.3</td>
<td>Q</td>
</tr>
<tr>
<td>91-74-2 600</td>
<td>2:1</td>
<td>33.3</td>
<td>Q</td>
</tr>
<tr>
<td>91-74-3</td>
<td>1.5:1</td>
<td>40</td>
<td>Q</td>
</tr>
<tr>
<td>91-75-1</td>
<td>0.9:1</td>
<td>52.6</td>
<td>G</td>
</tr>
<tr>
<td>MgTiO$_3$</td>
<td>0.9:1</td>
<td>52.6</td>
<td>G</td>
</tr>
</tbody>
</table>

Note: Q – qandilite, G – geikielite; Mg:Ti ratios and the TiO$_2$ mol % are based on the results from chemical analysis.

The normally high temperature phase qandilite was formed at a much lower temperature ($600 \, ^{0}\text{C}$) in our samples. According to the phase diagram shown in Figure 1, the qandilite phase is formed only above $1000 \, ^{0}\text{C}$ with a stoichiometry of Mg:Ti ratio 2:1. However, the nanocrystalline qandilite phase was found in samples with Mg:Ti ratios down to 1.53:1 different from the equilibrium structures which should have been created at high temperature. The formation of this metastable phase may
arise from the presence of nanocrystalline magnesia and titania in intimate contact. The diffusion process would take relatively short time in the range of about 20 nm (Zabicky et al., 1997).

Particle Size

The average particle sizes calculated from the refinement of neutron diffraction results using GSAS are listed in Table 11. Samples 91-74-2 600, 91-74-3 and with Mg:Ti ratios 2:1 and 1.5:1 have particle sizes around 10 nm while sample 91-75-1 with Mg:Ti ratio 0.9:1 has particle size smaller than 100 nm. All of them have particle size in the range of a nanocrystalline system while samples 91-74-2 1180 and MgTiO$_3$ have particle sizes in the range of a microcrystalline system. Samples obtained with metastable qandilite phases are assumed to be nonstoichiometric when compared to the samples obtained with stoichiometric phases (MgTiO$_3$) or the phases that were created at stable condition (91-74-2 1180).

Table 10

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>$\gamma_2$</th>
<th>p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgTiO$_3$</td>
<td>Geikielite</td>
<td>119.35</td>
<td>286</td>
</tr>
<tr>
<td>91-75-1</td>
<td>Geikielite</td>
<td>128.55</td>
<td>72</td>
</tr>
<tr>
<td>91-74-3</td>
<td>Qandilite</td>
<td>112.32</td>
<td>9</td>
</tr>
<tr>
<td>91-74-2 600</td>
<td>Qandilite</td>
<td>120.43</td>
<td>9</td>
</tr>
<tr>
<td>91-74-2 1180</td>
<td>Qandilite</td>
<td>14.32</td>
<td>174</td>
</tr>
</tbody>
</table>
Structures Refinement Results

Single Geikielite Phase

The parameters were determined by the final refinement of samples MgTiO$_3$ and 91-75-1. Both of them have Mg:Ti ratio of 0.9:1 and the refinement results are given in Table 11.

Table 11

<table>
<thead>
<tr>
<th></th>
<th>MgTiO$_3$ (0.9:1)</th>
<th>91-75-1 (0.9:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (nm)</td>
<td>0.506</td>
<td>0.505</td>
</tr>
<tr>
<td>$c_0$ (nm)</td>
<td>1.390</td>
<td>1.390</td>
</tr>
<tr>
<td>$V$ (nm$^3$)</td>
<td>0.308</td>
<td>0.307</td>
</tr>
<tr>
<td>$z$ (Mg)</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>$z$ (Ti)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$x$ (O)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$y$ (O)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$z$ (O)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Fraction (Mg)</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Fraction (Ti)</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Fraction (O)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$U_{iso}$ (Mg)</td>
<td>0.003</td>
<td>0.0030(7)</td>
</tr>
<tr>
<td>$U_{iso}$ (Ti)</td>
<td>0.002</td>
<td>-0.002</td>
</tr>
<tr>
<td>$U_{11}$ (O)</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>$U_{22}$ (O)</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>$U_{33}$ (O)</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>$U_{12}$ (O)</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>$U_{13}$ (O)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$U_{23}$ (O)</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>
The parameters that are shown for these two samples are quite similar although one has stoichiometric composition while the other may have nonstoichiometric composition. The reason might be that the qandilite phase is stable at room temperature so both are based on a stable phase although one is micro and the other is nano structure.

Sample 91-75-1 has lattice constants $a_0=0.505$ nm and $c_0=1.390$ nm which are the same as in a reference (Kimmel & Zabicky, 2000). The occupancy of cations is slightly different but quite close. The reference has relative composition fraction calculated from the refinement at Mg:Ti:O = 1:1:3 while ours has 0.9:0.8:3 based on GSAS. This description may be because our sample has the Mg:Ti ratio 0.9:1 (based on the chemical analysis). This may also result from the difference between the analysis using X-ray and neutron diffraction.

**Single Qandilite Phase**

The parameters from final refinements of samples 91-74-3, 91-74-2 600, 91-74-2 1180, which have Mg:Ti ratio of 1.53:1, 2:1, 2:1 respectively, are given in Table 12.
Table 12
Final Rietveld Refinements for Single Qandilite Phase

<table>
<thead>
<tr>
<th></th>
<th>91-74-3 (1.5:1)</th>
<th>91-74-2 600 (2:1)</th>
<th>91-74-2 1180 (2:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (nm)</td>
<td>0.843</td>
<td>0.843</td>
<td>0.843</td>
</tr>
<tr>
<td>$V$ (nm$^3$)</td>
<td>0.600</td>
<td>0.598</td>
<td>0.598</td>
</tr>
<tr>
<td>Fraction Ti:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oct</td>
<td>0.55</td>
<td>0.44</td>
<td>0.51</td>
</tr>
<tr>
<td>Tet</td>
<td>0.0</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>$U$ (O)</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>$U_{iso}$ Oct</td>
<td>0.01</td>
<td>-0.09</td>
<td>-0.05</td>
</tr>
<tr>
<td>Tet</td>
<td>-0.006</td>
<td>0.04</td>
<td>-0.03</td>
</tr>
<tr>
<td>$U_{11}$ (O)</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td>$U_{12}$ (O)</td>
<td>-0.00</td>
<td>0.00</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Note: $a_0$ = cell parameter; $U_{iso}$ = isotropic temperature factor; $U_{11}$ or $U_{12}$ = anisotropic temperature factor; Tet = tetrahedral site; Oct = octahedral site. The $U_{iso}$ values for cations in the same sites were constrained to be equal. Mg:Ti ratios given here are from chemical analysis.

The sample 91-74-3 and 91-74-2 600 are metastable phases because they were formed at 600 °C (well below their equilibrium conditions). The sample 91-74-2 1180, on the other hand, was formed at a stable condition (1180 °C for 6 hours). The
particle size that is calculated from γ₂ is much larger in 91-74-2 1180 than that in 91-74-2 600 (174 nm vs. 9 nm) as expected. Refinement results show no significant structural changes between metastable phases and the phase that was created at stable conditions.

Sample 91-74-2 1180 has lattice constant a₀ = 0.843 nm essentially the same as the reference value (a₀ = 0.844 nm). The occupancy of cations is slightly different from the reference at tetrahedral sites (0.03 vs. 0) and at octahedral sites (0.51 vs. 0.5). This may be a result of the heat treatment at different temperature. It may have also seemed this way because of the difference between X-ray and neutron diffraction.

The lattice constant of sample 91-74-3 and 91-74-2 600 is in agreement with the result of reference (Kimmel & Zabicky, 2000), which shows based on XRD that the unit cell remains constant over a wide range of Mg:Ti ratio.

X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy Results

The results of X-ray photoelectron spectra of samples MgTiO₃, 91-75-1, 91-74-3, 91-74-2 600, and 91-74-2 1180 which have the Mg:Ti ratio 0.9:1, 0.9:1, 1.5:1, 2:1, and 2:1 respectively are shown in Appendix B. The binding energy of Mg 2p, Mg 2s, Ti 2p₃/₂ and 2p₁/₂, and O 1s levels were scanned to check for the changes of the oxidation states of the cation and anions. The binding energy of C 1s in all samples is
used as a reference to calibrate the shifting from conduction potential and the external charges. The reference binding energy of C 1s is 285 eV. All the deviations are calculated from the binding energies that were already calibrated (see experimental description). The deviations of binding energy are shown in the Tables 13 and 14 for reference samples MgTiO$_3$ and 91-74-2 1180. The external charges are also listed. The main peak listed in the first row in Tables 13 and 14 gives the deviations in Figures 17 and 18.

The C 1s is composed of 2 or 3 peaks. The main peak was used for the calibration. It comes from the pumping oil and the air before vacuum process (Barr, 1994). The smaller peaks were from other C sources. Some carbons have come from the tape that is used to fix the position of powder sample. It could also be the residual C in organic compounds that were left during the sol-gel process. All the smaller peaks should not be considered for calibration because they have area much smaller than the main peak which makes the determination of their position doubtful.

The O 1s always has two peaks. The smaller peak that gives the asymmetry of the composed peak shape may come from the discontinuity of the crystal surface. It is always very close to the main peak or has very small area compared to the main peak. It may or may not belong to the structure so it is not reliable enough to consider. So only the main peaks should be considered.

The Mg 2p has two peaks. However, the smaller peak is from other split orbital. So the small peak should not be considered here.
Table 13

The Binging Energy Deviations from Reference Sample MgTiO₃ (eV)

<table>
<thead>
<tr>
<th>MgTiO₃ (0.9:1)</th>
<th>Ti 2p (eV)</th>
<th>O 1s (eV)</th>
<th>C 1s (eV) (calibration)</th>
<th>Mg2s (eV)</th>
<th>Mg2p (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charged: 2.543 eV</td>
<td>-0.121</td>
<td>-0.026</td>
<td>0</td>
<td>-0.08</td>
<td>-0.188</td>
</tr>
<tr>
<td>91-75-1 (0.9:1)</td>
<td>-0.105</td>
<td>*0.962</td>
<td>0</td>
<td></td>
<td>1.118</td>
</tr>
<tr>
<td>Charged: 2.015 eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: The second row is the deviation of small peaks that should not be considered (see text). Mg:Ti ratios are based on the result of chemical analysis.

Oxidation States of Geikielite Phase

Standard MgTiO₃ sample is a stoichiometric and stable phase. The prescribed charges of Mg, Ti, and O ions should be +2, +4, and -2 respectively. This sample is used as a reference to compare with 91-75-1 (0.9:1). C 1s values are zero in both samples indicating that both line position have been calibrated (Table 13).

The sample 91-75-1 may be a nonstoichiometric phase because it appears to have a ratio of Mg:Ti:O ratio 0.9:1:3.7. The deviation of the binding energy from the reference sample is relatively low so the oxidation state can be considered as consistent between these two samples. The titanium and magnesium cations did not show significant shift in oxidation state. This may be because the geikielite phase is stable at room temperature and the crystal structure is similar between these
stoichiometric and nonstoichiometric phases. The deviation is also shown in Figure 17 to illustrate the small deviations.

![Figure 17. Deviations of the Main Peaks of Sample 91-75-1 from Reference MgTiO₃.](image)

**Oxidation States of Qandilitite Phases**

The sample 91-74-2 1180 was formed at a stable condition compared with samples 91-74-2 600 and 91-74-3. So it is used as an internal reference to compare with other two samples. The deviations of the binding energy are shown in Table 14.
The significant changes of binding energy for titanium in both samples with metastable phases indicate that the oxidation state of titanium cation is changed. The reason for this is to keep charge balance. When less magnesium cations in the nonstoichiometric phase in 91-74-3, the titanium cations are reduced to lower oxidation state (closer to the oxidation state of magnesium cations) to keep the charge balanced. According to the reference (Richerson, 1992), the titanium cations is the only cation of the three in this system that could have more than one oxidation state (Ti$^{4+}$, Ti$^{3+}$, Ti$^{2+}$). A comparison chart illustrates the deviations shown in Figure 18.

Compared with 91-74-2 1180, 91-74-2 600 have titanium cations with lower oxidation state. This may be due to possible nonstoichiometry based on the chemical analysis results.
Figure 18. Comparison of Samples 91-74-3 & 91-74-2 1180 with the Reference Sample 91-74-2 1180.
CHAPTER V

CONCLUSIONS

The powder of magnesium titanates that were synthesized at 600 °C have particle size much smaller than 100 nm indicating that they are all in the nanometric range. Chemical analysis shows that all nanocrystalline powders may have nonstoichiometric ratios of Mg:Ti:O. However, the nanocrystalline powders with Mg:Ti ratio 0.9:1, 2:1, and 1.5:1 were observed as having the same crystal structure as those in the micro sized geikielite and qandilite phases that were formed at equilibrium state. The mass loss during the chemical analysis gives rise to the assumption that excess oxygen may have come from outside the structure.

Compared to a commercial MgTiO$_3$ powder that has a stable single geikielite phase with micro size crystals, nanocrystalline geikielite shows no significant change of either structure or oxidation states. However, the nanocrystal geikielite sample appears as to have the Mg:Ti:O ratio 0.9:1:3.7 based on the chemical analysis. The excess oxygen may have come from outside the structure. Other concentration variations could be residual organic or polymers from the sol-gel process. This possibility is farther reinforced by the mass loss from chemical analysis.

Compared to the microcrystalline qandilite phase which was formed at equilibrium (1180 °C), nanocrystalline qandilite with Mg:Ti ratio 1.5:1 and 2:1 were obtained with no significant structure changes but with oxidation states changes of the titanium cations. In the sample with Mg:Ti 1.5:1, we have lower Mg ratio than the
stoichiometric one which means we have too much titanium cations. This will cause the compound to have too much positive charge. To avoid this extra positive charge, the oxidation state of titanium cations changes to a more reduced state (i.e. $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ or $\text{Ti}^{2+}$) then the total charges of the compound is kept balanced. It is a bit less obvious for the sample with Mg:Ti ratio 2:1, as the proportions of Mg:Ti are as in a stoichiometric one. However, the lack of known values for the amount of oxygen in the structure suggests that this sample is nonstoichiometric as well.

Metastable nanocrystalline phases of qandilite were formed at 600 °C, a temperature which is much lower than the equilibrium state (1180 °C) and had lower Mg:Ti ratios even down to 1.5:1, similar to XRD results in reference (Kimmel & Zabicky, 2000). The ratio is based on the results from chemical analysis. However, the structure refinement results from GSAS are in conflict with this Mg:Ti ratio. According to the above reference (Kimmel & Zabicky, 2000), the Mg:Ti ratio can be even 1.3:1 for single qandilite phase.
CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

Chemical analysis should be performed for sample 91-74-2 1180 that have the equilibrium single qandilite phase in order to check whether the Mg:Ti:O ratio is stoichiometric or not. Also, the chemical analysis for all samples should trace all magnesium, titanium, oxygen, and carbon ions rather than magnesium and titanium cations only.

In order resolve the conflict with the chemical analysis, the structure refinement of GSAS may be redone with different basic assumptions (e.g. assuming tetragonal structure).

The analysis of surface composition can be done from XPS results. This will give more detailed information of the difference between the surface and the bulk material.
Appendix A

Neutron Powder Diffraction Profiles
Figure A-1. Neutron Powder Diffraction Profiles of Sample MgTiO₃
Figure A-2. Neutron Powder Diffraction Profiles of Sample 91-75-1
Figure A-3. Neutron Powder Diffraction Profiles of Sample 91-74-3
Figure A-4. Neutron Powder Diffraction Profiles of Sample 91-74-2 600
Figure A-5. Neutron Powder Diffraction Profiles of Sample 91-74-2 1180
Appendix B

X-ray Photoelectron Spectroscopy Spectra
Figure B-1. Ti 2p X-ray Photoelectron Spectra in MgTiO₃
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>533.256</td>
<td>27561.66</td>
<td>3.216</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>532.421</td>
<td>24046.74</td>
<td>1.479</td>
<td>16%</td>
</tr>
</tbody>
</table>

Figure B-2. O 1s X-ray Photoelectron Spectra in MgTiO$_3$. 
MgTiO3 (A)

C1s

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>287.453</td>
<td>7489.719</td>
<td>1.908</td>
<td>54%</td>
</tr>
<tr>
<td>8</td>
<td>291.695</td>
<td>208.006</td>
<td>1.276</td>
<td>26%</td>
</tr>
</tbody>
</table>
Figure B-4. Mg 2s X-ray Photoelectron Spectra in MgTiO₃
Figure B-5. Mg 2p X-ray Photoelectron Spectra in MgTiO₃
Figure B-6. Ti 2p X-ray Photoelectron Spectra in 91-75-1
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>532.957</td>
<td>44147.420</td>
<td>1.747</td>
<td>27%</td>
</tr>
<tr>
<td>4</td>
<td>534.780</td>
<td>4023.280</td>
<td>1.553</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure B-7. O 1s X-ray Photoelectron Spectra in MgTiO₃
Figure B-8. 1s X-ray Photoelectron Spectra in 91-75-1
Figure B-9. Mg 2s X-ray Photoelectron Spectra in 91-75-1
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area (arb. units)</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>39.991</td>
<td>4435.160</td>
<td>2.276</td>
<td>54%</td>
</tr>
<tr>
<td>10</td>
<td>41.570</td>
<td>466.951</td>
<td>2.711</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure B-10. Mg 2p X-ray Photoelectron Spectra in 91-75-1
Figure B-11. Ti 2p X-ray Photoelectron Spectra in 91-74-3
Figure B-12. O 1s X-ray Photoelectron Spectra in 91-74-3
Figure B-13. C 1s X-ray Photoelectron Spectra in 91-74-3
Figure B-14. Mg 2s X-ray Photoelectron Spectra 91-74-3
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>40.194</td>
<td>3107.52</td>
<td>2.550</td>
<td>32%</td>
</tr>
<tr>
<td>10</td>
<td>42.924</td>
<td>238.892</td>
<td>1.746</td>
<td>29%</td>
</tr>
</tbody>
</table>

Figure B-15. Mg 2p X-ray Photoelectron Spectra in 91-74-3
Figure B-16. Ti 2p X-ray Photoelectron Spectra in 91-74-2 600
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>534.8654</td>
<td>5817.684</td>
<td>1.752eV</td>
<td>4%</td>
</tr>
<tr>
<td>4</td>
<td>534.0211</td>
<td>14427.660</td>
<td>3.595eV</td>
<td>0%</td>
</tr>
<tr>
<td>5</td>
<td>532.936eV</td>
<td>29818.250</td>
<td>1.840eV</td>
<td>25%</td>
</tr>
</tbody>
</table>

Figure B-17. O 1s X-ray Photoelectron Spectra in 91-74-2 600
### Table of C 1s X-ray Photoelectron Spectra

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area (arb. units)</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>292.800</td>
<td>538.563</td>
<td>2.180</td>
<td>0%</td>
</tr>
<tr>
<td>10</td>
<td>287.805</td>
<td>3593.832</td>
<td>1.822</td>
<td>70%</td>
</tr>
<tr>
<td>11</td>
<td>287.328</td>
<td>1223.286</td>
<td>2.592</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure B-18. C 1s X-ray Photoelectron Spectra in 91-74-2 600
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position</th>
<th>Area</th>
<th>FWHM</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>91.638eV</td>
<td>6131.700</td>
<td>2.390eV</td>
<td>26%</td>
</tr>
</tbody>
</table>

Figure B-19. Mg 2s X-ray Photoelectron Spectra in 91-74-2 600
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>40.163</td>
<td>1537.947</td>
<td>1.879</td>
<td>80%</td>
</tr>
<tr>
<td>8</td>
<td>40.498</td>
<td>1598.146</td>
<td>3.551</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure B-20. Mg 2p X-ray Photoelectron Spectra in 91-74-2 600
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>461.695eV</td>
<td>22647.880</td>
<td>1.628eV</td>
<td>31%</td>
</tr>
<tr>
<td>1</td>
<td>467.358eV</td>
<td>11944.830</td>
<td>2.125eV</td>
<td>80%</td>
</tr>
</tbody>
</table>

Figure B-21. Ti 2p X-ray Photoelectron Spectra in 91-74-2 1180
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>532.474</td>
<td>21916.880</td>
<td>1.813</td>
<td>31%</td>
</tr>
<tr>
<td>9</td>
<td>534.400</td>
<td>4512.058</td>
<td>1.922</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure B-22. O 1s X-ray Photoelectron Spectra in 91-74-2 1180
Figure B-23. C 1s X-ray Photoelectron Spectra in 91-74-2 1180
Figure B-24. Mg 2s X-ray Photoelectron Spectra in 91-74-2 1180
<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Area</th>
<th>FWHM (eV)</th>
<th>%GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>39.782</td>
<td>1396.207</td>
<td>2.094</td>
<td>38%</td>
</tr>
<tr>
<td>10</td>
<td>40.220</td>
<td>1088.360</td>
<td>4.717</td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure B-25. Mg 2p X-ray Photoelectron Spectra in 91-74-2 1180
BIBLOGRAPHY


Kenneth J. Klabunde (2001). *Nanoscale materials in chemistry*


