QUANTITATIVE X-RAY DIFFRACTOMETRY AND STRUCTURAL ANALYSIS OF MAGNESIUM TITANATE MIXTURES USING THE RIETVELD REFINEMENT

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ABSTRACT

Nanometric precursors that were prepared by sol-gel methods consist of hydroxides of magnesium and titanium, which lose water on heating to about 400°C, yielding nanocrystalline oxides. Geikielite, qandilite and karrooite are formed from coprecipitated precursor powder at about 600°C, depending on the relative stoichiometry of magnesia and titania in the precursor. However, from about 700°C up to about 1200°C qandilite and karrooite decompose, leaving geikielite as the only stable titanate, and they reappear as stable phases at about 1300°C or higher temperatures, depending on the stoichiometry of the original mixture.

XRPD analysis was the main research tool for the thermal behavior of the magnesia-titania system. At the lower temperatures single phase products were obtained. These structures tolerated large deviation from stoichiometry. Rietveld structural analysis was used to refine the unusual ion occupancies. Rietveld quantitative analysis was conducted in order to evaluated the amount of amorphous phase, using an internal standard. Above 700°C the Rietveld structural results showed fully crystalline and stoichiometric phases. Relative mass amounts were also derived by the Rietveld method. The results were well supported by chemical analysis. This study demonstrates the strength of the full pattern treatment for XRPD characterization of solid powders.

INTRODUCTION

The magnesium titanates are important as ceramic industrial materials. There are three intermediate phases between MgO and TiO₂: 2MgO·TiO₂ (qandilite), Mg₃O₂·TiO₂ (geikielite), and MgO·2TiO₂ (karrooite). It is possible to form these phases by reactions between MgO and TiO₂ powders at high temperature. The temperature are dictated by the phase diagram and the kinetics. According to Wechsler and Navrotsky [1] only the geikielite is stable at room temperature and the qandilite and geikielite exist in equilibrium only at high temperatures. The qandilite and geikielite are supposed to decompose at lower temperatures by eutectoid reactions. The eutectoid temperature is higher for qandilite. The exact eutectoid temperatures have not been determined yet.

Nanometric precursors that were prepared by sol-gel methods consist of hydroxides of magnesium and titanium, which lose water on heating to about 400°C, yielding nanocrystalline oxides. Geikielite, qandilite and karrooite are formed from coprecipitated precursor powder at about 600°C, depending on the relative stoichiometry of magnesia and titania in the precursor [2]. However, from about 700°C up to about 1100°C qandilite and karrooite decompose, leaving geikielite as the only stable titanate, and they reappear as stable phases at about 1200°C or higher temperatures, depending on the stoichiometry of the original mixture [1].
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The crystal structures of the intermediate phases is well established [3], following early studies of qandilite [4-6], geikielite [7-9], and karrooite [10,11]. The karrooite structures tolerate some deviation from stoichiometry due to disordering in the ionic occupation as a function of temperature [1,3,11].

The coprecipitated precursor powders can serve as homogeneous materials for studying the equilibrium phase diagram of the system MgO-TiO$_2$. In order to complete a full phase diagram study it was decided to prepare more than 20 compositions of pMgO.qTiO$_2$ and characterize the structure after various thermal treatments.

XRPD analysis was the main research tool for the thermal behavior of the magnesia-titania system. Rietveld refinement was utilized for studying the ion occupancies, cell parameters and to evaluate relative phase amounts. For the measuring of the amount of amorphous phase, an internal standard was added.

**Crystal Structures**

The system MgO-TiO$_2$ consists of five fundamental structures, as listed in table 1.

<table>
<thead>
<tr>
<th>our label</th>
<th>phase</th>
<th>chemical formula</th>
<th>Pearson symbol</th>
<th>Crystal type</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>periclase</td>
<td>MgO</td>
<td>cF8</td>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>qandilite</td>
<td>Mg$_2$TiO$_4$</td>
<td>cF56</td>
<td>Al$_2$MgO$_4$</td>
<td>H.T. phase</td>
</tr>
<tr>
<td>G</td>
<td>geikielite</td>
<td>Mg$_3$TiO$_3$</td>
<td>hR10</td>
<td>FeTiO$_3$</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>karrooite</td>
<td>MgTi$_2$O$_5$</td>
<td>aC32</td>
<td>Fe$_2$TiO$_3$</td>
<td>H.T. phase</td>
</tr>
<tr>
<td>R</td>
<td>rutile</td>
<td>TiO$_2$</td>
<td>tP6</td>
<td>TiO$_2$</td>
<td></td>
</tr>
</tbody>
</table>

Qandilite and karrooite are stable at high temperatures above 1150°C. After formation at high temperature and quenching the compounds maintain the high temperature structure at room temperature. The Mg$^{2+}$ and Ti$^{4+}$ cations share the same atomic positions. Thermal annealing at a temperature range above 500°C modify the atomic positions and occupancies as well as the cell parameters.

**EXPERIMENTAL**

Twenty six samples of Mg:Ti atomic ratios ranging from 1:4 to 4:1 were prepared. A primary thermal treatment for all samples was performed at 600°C for 3 hours.

Secondary thermal treatments were conducted to samples with a constant Mg:Ti atomic ratio of 1.75:1 at temperatures ranging from 600°C to 1500°C, for 3 hours. Another secondary treatment made to a sample with atomic ratio of Mg:Ti = 1.2 at 1500°C for 3 hours.

All samples were tested by XRD and refined by Rietveld method. Additional quantitative analysis was conducted to the samples with the secondary thermal treatments, in order to evaluated the amount of amorphous phase, using an internal standard - corundum.

The XRD system was Philips PW3720 0/2θ diffractometer with Cu anode and graphite monochromator attached to the detector. The instrument was operated in the following conditions: Power: 40KV, 40mA; scanning parameters: 2θ range: from 12 to 158°; typical 2θ step size: 0.02°, measuring time: 1 to 5 seconds per step. Quantitative phase
analysis and structure refinement was performed by Rietveld method, using DBWS-9411 software [12].

RESULTS AND DISCUSSION

Qualitative and quantitative analysis

Samples after 3 hours at 600°C:

Five phases were identified along the entire concentration range.

Half of the samples were obtained as pure phases in three Mg/Ti ranges. Between the Mg/Ti ratios of 2:1 to 1.3:1 a pure cubic spinel (qandilite) was found. The geikielite found as a pure phase only at Mg/Ti =1. A pure karrooite phase was found in Mg/Ti range of 1:1.6-1:2. The ranges of the pure phases is shown in Table 2.

Table 2: Mg/Ti ranges of pure phases after thermal annealing at 600°C for 3 h

<table>
<thead>
<tr>
<th>Mg/Ti range</th>
<th>qandilite</th>
<th>geikielite</th>
<th>karrooite</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 - 1.3:1</td>
<td>1:1</td>
<td>1:1.6 - 1:2</td>
<td></td>
</tr>
<tr>
<td>atomic % of Ti in the cations</td>
<td>33.3 - 43.5</td>
<td>50.0</td>
<td>61.5 - 66.7</td>
</tr>
</tbody>
</table>

Half of the samples were found with a mixture of two phases. The list of the phases in along the Mg/Ti ratios is given in Table 3. Typical samples with quantitative analysis of the mixtures are given in table 4.

Table 3: List of mixtures in the MgO-TiO2 system after 600°C for 3 hours

<table>
<thead>
<tr>
<th>Mg/Ti ratio</th>
<th>phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>ratio &gt; 2:1</td>
<td>periclase and qandilite</td>
</tr>
<tr>
<td>1.3:1 &gt; ratio &gt; 1:1</td>
<td>qandilite and geikielite</td>
</tr>
<tr>
<td>1:1 &gt; ratio &gt; 1:1.6</td>
<td>geikielite and karrooite</td>
</tr>
<tr>
<td>1:2 &gt; ratio</td>
<td>karrooite and rutile</td>
</tr>
</tbody>
</table>

Table 4: Amounts of phases in selected samples after 600°C for 3 hours

<table>
<thead>
<tr>
<th>phases</th>
<th>PQ</th>
<th>PQ</th>
<th>PQ</th>
<th>QG</th>
<th>QG</th>
<th>GK</th>
<th>GK</th>
<th>GK</th>
<th>GK</th>
<th>CR</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/Ti ratio</td>
<td>4:1</td>
<td>3:1</td>
<td>2.1:1</td>
<td>1.2:1</td>
<td>1:1:1</td>
<td>1:1.2</td>
<td>1:1.3</td>
<td>1:1.4</td>
<td>1:1.5</td>
<td>1:3</td>
<td>1:4</td>
</tr>
<tr>
<td>phase amount</td>
<td>51</td>
<td>32.5</td>
<td>8</td>
<td>4.3</td>
<td>9.4</td>
<td>9.6</td>
<td>21</td>
<td>33</td>
<td>40</td>
<td>14.5</td>
<td>28</td>
</tr>
<tr>
<td>mol % of</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>K</td>
<td>K</td>
<td>K</td>
<td>K</td>
<td>R</td>
<td>R</td>
</tr>
</tbody>
</table>

Sample with atomic ratio of Mg:Ti = 1.75 after secondary thermal treatments:

The qualitative and quantitative results are shown in Table 5. After the primary treatment a single phase of non-stoichiometric qandilite was obtained as expected from Table 2. This structure remained as a single phase up to 700°C and started to decompose at 800°C to geikielite and periclase. The qandilite XRD diffraction lines of these samples were severely broadened. From line profile analysis, a mean crystallite size of 7 nm and internal strain \(<\varepsilon^2>^{1/4}\) of 0.2-0.3% were estimated. The amount of amorphous phase decreased from 10 wt. % for treatment at 600°C to 4% in sample treated at 800°C.
Between 900°C and 1100°C the major phases were geikielite and periclase with several percents of retained qandilite. At 1200°C the qandilite reappeared as a major phase and most of the periclase disappeared. From 1300°C and up the system was stable with 75 mole % of qandilite and the rest was geikielite. It should be noticed that above 900°C the XRD spectra became sharp, the amount of phases obeyed the level rule for the atomic ratio of Mg:Ti = 1.75, and there was no amorphous phase.

According to Wechsler and Navrotsky [1] the eutectoid temperature for qandilite is between 1100 and 1500 K. In our work, the kinetics hindered the decomposition of the qandilite only till 700°C. From 900°C the system is close to equilibrium. According to the present study the qandilite eutectoid temperature is in the range between 1400 to 1500 K.

Table 5: Qualitative and quantitative analysis of gel with atomic ratio of Mg:Ti = 1.75

<table>
<thead>
<tr>
<th>annealing temperature [°C]</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1500</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>qandilite mole %</td>
<td>100</td>
<td>100</td>
<td>76</td>
<td>7</td>
<td>4</td>
<td>3</td>
<td>62</td>
<td>75</td>
<td>72</td>
<td>76</td>
<td>74</td>
</tr>
<tr>
<td>geikielite mole %</td>
<td>-</td>
<td>-</td>
<td>22</td>
<td>56</td>
<td>58</td>
<td>57</td>
<td>24</td>
<td>25</td>
<td>28</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td>Periclase mole %</td>
<td>-</td>
<td>-</td>
<td>37</td>
<td>38</td>
<td>40</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>amorphous phase wt %</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Structure analysis in regions of pure phases

Qandilite (cubic):

The qandilite found as a cubic single phase in a range of Mg:Ti ratio (2:1-1:1.1). There was no change in the unit cell dimensions versus the Mg:Ti ratio. The formula Mg$_{2-x}$TiO$_4$ seems to be better than the first choice for non-stoichiometric compound (Mg$_{2-x}$Ti$_{1-x}$O$_4$). The refined crystallographic data for Mg:Ti = 1.7 is given in Table 6. The profile assumed as pseudo-Voigt, 75% Lorentzian and 75% Gaussian. The line width found to be expressed by:

FWHM ($2\theta$) = (0.945 + 0.246 tan$\theta$ + 1.2 tan$\theta^2$)$^{0.5}$

All samples treated at 600°C exhibit broadened diffraction spectra, including samples with Mg:Ti = 2. Thus, the broadening effect is not associated with the deviation from stoichiometry. Moreover, the deficiency of magnesium was found even in sample with Mg:Ti = 2 where periclase appeared as a second phase. Hence, this nanostructure should be regarded as a special metastable structure, and more study should be done to complete the knowledge about it.

Table 6: Refinement results for Mg$_{1.7}$TiO$_4$ - after thermal treatment of xerogel at 600°C

<table>
<thead>
<tr>
<th>positions</th>
<th>relative occupancy</th>
<th>isotropic thermal factor [Å$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) Mg1</td>
<td>0.835</td>
<td>0.524</td>
</tr>
<tr>
<td>(d) Ti</td>
<td>1.0</td>
<td>0.524</td>
</tr>
<tr>
<td>(a) Mg2</td>
<td>0.865</td>
<td>0.215</td>
</tr>
<tr>
<td>(c) O (0.2602)</td>
<td>4</td>
<td>0.541</td>
</tr>
</tbody>
</table>
Above 700°C the qandilite could be refined as stoichiometric cubic structure. Table 7 shows the structural parameters of Mg₂TiO₄ after secondary treatment at 1300°C. The values are close to the neutron diffraction data for the cubic qandilite [3]. The profile was assumed as pseudo-Voigt, 28% Lorentzian and 72% Gaussian. The line width found to be sharp:

\[
\text{FWHM (2θ)} = (0.0281 - 0.0314 \tan\theta + 0.0284 \tan^2\theta)^{0.5}
\]

Table 7: Refinement results for Mg₂TiO₄ after secondary annealing at 1300°C

<table>
<thead>
<tr>
<th>positions</th>
<th>Relative occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) Mg⁺</td>
<td>1</td>
</tr>
<tr>
<td>(d) Ti</td>
<td>1</td>
</tr>
<tr>
<td>(a) Mg²</td>
<td>1</td>
</tr>
<tr>
<td>(e) O (0.260)</td>
<td>4</td>
</tr>
</tbody>
</table>

Geikielite (rhombohedral):

The geikielite was obtained in the same structure at all temperatures. There was no deviation from stoichiometry. An example of Rietveld refinement results is given in Table 8. The results confirm the last reported data from neutron diffraction [3]. The diffraction patterns showed broadening effects in samples treated at 600°C. There was no broadening effect in diffraction of geikielite which has been formed at 1200°C and up.

Table 8: Refinement results for MgTiO₃

<table>
<thead>
<tr>
<th>positions</th>
<th>Relative occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c) Mg (0.3554)</td>
<td>1</td>
</tr>
<tr>
<td>(c) Ti (0.1449)</td>
<td>1</td>
</tr>
<tr>
<td>(f) O (0.3163;0.02148;0.2459)</td>
<td>3</td>
</tr>
</tbody>
</table>

For sample treated at 600°C the profile was assumed as pseudo-Voigt, 43.2% Lorentzian and 66.2% Gaussian. The line width found to be sharp:

\[
\text{FWHM (2θ)} = (0.0927 - 0.2125 \tan\theta + 0.2298 \tan^2\theta)^{0.5}
\]

For sample treated at 1300°C the profile assumed as pseudo-Voigt, 27% Lorentzian and 73% Gaussian. The line width found to be sharp:

\[
\text{FWHM (2θ)} = (0.0131 - 0.0208 \tan\theta + 0.0263 \tan^2\theta)^{0.5}
\]
Karrooite (orthorhombic):

In samples of 1-Mg:Ti<0.5 treated at 600°C, the deviation from stoichiometry is obtained differently than in qandilite. In karrooite the cations are completely mixed. Hence, the chemical formula becomes Mg_{1+x}Ti_{2-x}O_5 (0<x<0.5). The stoichiometry is strongly correlated with irregularities in cation occupancies. In contrast to qandilite, the unit cell of karrooite was modified according to the deviation from stoichiometry. The deviation of the cell parameter from the stoichiometric karrooite was much beyond the cell parameter shifts reported in the literature [1,3]. Crystal data of a typical non-stoichiometric sample is shown in Table 9. The profile assumed as pseudo-Voigt, 70% Lorentzian and 30% Gaussian. The line width found to be slightly broadened:

FWHM (2θ°) = (0.049 + 0.086 tanθ + 0.130 tanθ^2 )^{0.5}

Table 9: Refinement results for Mg_{1.2}Ti_{1.8}O_5 - primary treatment of xerogel at 600°C

<table>
<thead>
<tr>
<th>cell parameters: a=0.3753 nm; b=0.9744 nm; c=0.9952 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group Cmcm (63)</td>
</tr>
<tr>
<td>origin at center (2/m)</td>
</tr>
<tr>
<td>positions</td>
</tr>
<tr>
<td>(c) Mg1 (y=0.188)</td>
</tr>
<tr>
<td>(c) Ti1 (y=0.188)</td>
</tr>
<tr>
<td>(f) Mg2 (y=0.14;z=0.568)</td>
</tr>
<tr>
<td>(f) Ti2 (y=0.14;z=0.568)</td>
</tr>
<tr>
<td>(c) O1 (y=0.73)</td>
</tr>
<tr>
<td>(f) O2 (y=0.04;z=0.115)</td>
</tr>
<tr>
<td>(f) O3 (y=0.31;z=0.073)</td>
</tr>
</tbody>
</table>

Structural data of karrooite after a secondary treatment at 1500°C is shown in Table 10. The values are close to the previous data for the orthorhombic karrooite [1,3]. The profile assumed as pseudo-Voigt, 28% Lorentzian and 72% Gaussian. The line width found to be sharp:

FWHM (2θ°) = (0.0093 - 0.0083 tanθ + 0.0126 tanθ^2 )^{0.5}

Table 10: Refinement results for of Mg:Ti=0.5 xerogel after secondary treatment at 1500°C for 3h

<table>
<thead>
<tr>
<th>cell parameters: a=0.3745 nm; b=0.9742 nm; c=0.9991 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group Cmcm (63)</td>
</tr>
<tr>
<td>origin at center (2/m)</td>
</tr>
<tr>
<td>positions</td>
</tr>
<tr>
<td>(c) Mg1 (y=0.192)</td>
</tr>
<tr>
<td>(c) Ti1 (y=0.192)</td>
</tr>
<tr>
<td>(f) Mg2 (y=0.136;z=0.564)</td>
</tr>
<tr>
<td>(f) Ti2 (y=0.136;z=0.564)</td>
</tr>
<tr>
<td>(c) O1 (y=0.769)</td>
</tr>
<tr>
<td>(f) O2 (y=0.046;z=0.1118)</td>
</tr>
<tr>
<td>(f) O3 (y=0.31;z=0.073)</td>
</tr>
</tbody>
</table>
SUMMARY AND CONCLUSIONS

Samples which have been prepared in sol-gel technique in the MgO-TiO₂ system

1. In the atomic ratios of Mg:Ti between 2:1 to 1.3:1 a single qandilite phase was observed. The qandilite is a major phase with only some percent of geikielite. In the atomic ratios of Mg:Ti between 1.3:1 to 1.1:1, the cell parameter of was normal with a constant value of 0.844 nm, but the diffraction lines were severely broadened.

2. Between 800°C and 1100°C the qandilite decomposes into geikielite and periclase. The qandilite reappears at 1200°C as a stoichiometric structure (Mg:Ti = 2:1). The diffraction lines are sharp. Hence, the eutectoid temperature of qandilite is in temperature range between 1370 to 1470 K.

3. In the atomic ratios of Mg:Ti between 1:1.6 to 1:2 a single karrooite phase was observed. In contrast to the sudden fall of the amount of qandilite near Mg:Ti = 1, the amount of geikielite decreases gradually in the range of Mg:Ti between 1:1.1 to 1:1.3.

4. The unit cell of karrooite is modified according to the deviation from stoichiometry.

5. The diffraction lines of karrooite annealed at 600°C are broadened, but less severely than qandilite.

6. The deviation from stoichiometry is obtained differently in karrooite and in qandilite. In karrooite the cations are mixed forming Mg₁ₓT₂₋ₓO₅ structure. In qandilite treated at 600°C the deviation from stoichiometry obtained by vacancies of magnesium. The chemical formula becomes: Mg₂₋ₓTiO₄.

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