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# Stearic acid gel derived MgTiO $_3$ nanoparticles: A low temperature intermediate phase of Mg $_2$ TiO $_4$

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#### A R T I C L E I N F O

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#### ABSTRACT

Stearic acid gel is employed to study the phase evolution of MgTiO<sub>3</sub> nanoparticles by thermal gravimetric analysis, X-ray diffraction, and Fourier transform infrared. During the preparation of stearic acid gel, tetrabutyl titanate easily absorbed moisture to hydrolyze into  $Ti(OH)_4$  firstly, and then reacts with stearic acid and magnesium stearate to form magnesium–titanium oxide network polymer gel, meanwhile n-butanol is generated. When stearic acid gel is calcined in air, a series of oxidation and combustion reactions occur, meanwhile apparent heat is given off. The results show that a metastable intermediate phase  $Mg_2TiO_4$  is generated at 450 °C and nearly disappeared at 550 °C. Simultaneously, a new solid phase of  $MgTiO_3$  appears. The metastable intermediate phase  $Mg_2TiO_4$  is successfully identified in the current work.

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#### 1. Introduction

Magnesium titanate (MgTiO<sub>3</sub>), with ilmenite structure, has the dielectric properties of low dielectric loss (high quality factor), high dielectric constant and near zero temperature coefficient of resonant frequency [1]. Therefore, MgTiO<sub>3</sub> has wide applications in capacitors, resonators, filters, antennas for communication, radar, direct broadcasting satellite and global positioning system operating at microwave frequencies [2,3]. In the past thirty years, much attention has been focused on the synthesis of MgTiO<sub>3</sub>. Various synthesis methods are reported, including physical and chemical methods [4-9]. In particular, stearic acid gel (SAG) method is a useful and attractive method for synthesis of MgTiO<sub>3</sub> nanoparticles. In a recent report on SAG synthesis of MgTiO<sub>3</sub> powders by Kang et al. [10], the tetragonal flake-like nanocrystallites of MgTiO<sub>3</sub> is synthesized by SAG method. SAG method has also many distinctive advantages to prepare nanoparticles of BaTiO<sub>3</sub> [11,12] and ZnTiO<sub>3</sub> [13], such as decreasing significantly the crystallization temperature, producing high purity nanopowders, easy control of the M (M = Ba, Zn and Mg) and Ti stoichiometric ratio and low cost in comparison with other sol-gel methods [11,12].

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Recently, most studies mainly focus on improving the purity and reducing sintering temperature of MgTiO<sub>3</sub> ceramic powder. To improve the purity of MgTiO<sub>3</sub>, investigating the phase evolution of MgTiO<sub>3</sub> nanoparticles is very meaningful. In the past decades, there were some reports related to intermediate phases to produce MgTiO<sub>3</sub> by various methods. For the first kind of the solid-state reaction method, an intermediate phase of MgTi<sub>2</sub>O<sub>5</sub> was observed during the reaction process [14,15]. For the second kind of the acetic acid sol-gel method, the intermediate phases like MgTi<sub>2</sub>O<sub>5</sub>, Mg<sub>2</sub>TiO<sub>4</sub> and TiO<sub>2</sub> were appeared during the thermal decomposition of the gel [2,16]. For the third kind of the coprecipitation method, the product was never completely free from the phase of MgTi<sub>2</sub>O<sub>5</sub> [17]. For the last kind of the mechano-chemical complexation method, the phase of MgTi<sub>2</sub>O<sub>5</sub> was observed in the final product of MgTiO<sub>3</sub> [18]. Up to now, no work was on the phase evolution of SAG to produce MgTiO<sub>3</sub>.

The aim of this work is to determine the mechanism of SAG thermal decomposition and to obtain the optimum conditions for producing high purity  $MgTiO_3$  nanoparticles. Different measures including calcination of SAG, blank experiment and quenching method are employed to uncover the mechanism of  $MgTiO_3$  nanoparticles derived from SAG. Especially,  $MgTiO_3$  nanoparticles are evolved through a metastable intermediate phase  $Mg_2TiO_4$ , which appears at 450 °C and disappears at 550 °C. Furthermore, 600 °C is the optimal temperature to mildly synthesize  $MgTiO_3$  nanoparticles.

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Scheme 1. All steps of investigating the phase evolution of MgTiO<sub>3</sub> nanoparticles.

#### 2. Experimental

#### 2.1. Gel preparation procedure

The gel was prepared by using available manufacture of analytical grade magnesium stearate, tetrabutyl titanate, and stearic acid. An appropriate amount of stearic acid was first melted in a beaker at about 100 °C, and then a fixed amount of magnesium stearate was added to the melted stearic acid and dissolved to form a yellow transparent solution. Subsequently, the stoichiometric tetrabutyl titanate was added to this solution under stirring to form a homogeneous brown sol. At the same time some little bubbles were generated in the brown sol. Treated the brown sol at high temperature for short time to remove the little bubbles into the air. And then naturally cooled down to room temperature, finally, dried for 12 h to obtain the gel denoted as "Mg–Ti gel". The Mg–Ti gel was calcined at different temperatures in air to obtain samples. In a typical synthesis procedure, stearic acid, magnesium stearate and tetrabutyl titanate were mixed according to the molar ratio [stearic acid]:[magnesium stearate]:[tetrabutyl titanate] = 2.1:1.0:1.0.

To investigate the possible reactions occurred in the preparation of Mg–Ti gel, the generated little bubbles caused by adding tetrabutyl titanate were cooled into distillate by a condenser in the other similar preparation of Mg–Ti gel experiment, and analyzed the transparent distillate by FTIR.

Keeping the same conditions as the above "Mg–Ti gel" preparation, blank experiments were carried out for only the Mg or Ti component dissolved in stearic acid to form the corresponding gels, denoted as "Mg gel" or "Ti gel".

#### 2.2. Characterization

The thermal decomposition of the dried Mg–Ti gel was analyzed by thermogravimetric analyzer (TGA, TGA/SDTA 851<sup>e</sup>, Switzerland). TGA/SDTA measurements were done from room temperature to 600 °C with a heating rate of 10 °C/min in air. The calcined powders were characterized by X-ray diffraction (XRD, D/Max-3C, Japan), using Cu K $\alpha$  radiation. FTIR spectra of the obtained samples were characterized by Fourier transform infrared spectrometry (FTIR, Bruker Equinox 55, Germany), using KBr as a binding material in the range of  $400-4000 \text{ cm}^{-1}$ . The general morphology of MgTiO<sub>3</sub> nanoparticles was detected by transmission electron microscopy (TEM, Tecnai G220 S-Twin, America). The average and distribution sizes of MgTiO<sub>3</sub> nanoparticles were calculated from MgTiO<sub>3</sub> transmission electron images by the software of Gatan Digital Micrograph.

#### 2.3. Scheme on investigating the phase evolution of MgTiO<sub>3</sub> nanoparticles

In the current work, many measures were taken to investigate the phase evolution of  $MgTiO_3$  nanoparticles, to clearly show all steps here, they were summarized in Scheme 1. Scheme 1 clearly shows that three kinds of gel were prepared, and a series of characterizations were carefully carried out.

#### 3. Results and discussion

#### 3.1. Thermal decomposition process

Fig. 1 shows the TGA-SDTA analysis for the dried Mg–Ti gel. For the SDTA curve in Fig. 1, the endothermic peak at 110 °C is assigned to the volatilization of generated n-butanol. All other peaks are exothermal over 170 °C. This means that the decomposition process of the Mg–Ti gel consists of a series of oxidation and combustion reactions. The TGA curve in Fig. 1 indicates that the weight loss occurs in three steps corresponding to their exothermal peaks (at 322, 418 and 465 °C in the SDTA curve): (i) the initial weight loss of about 46% occurs from 170 to 330 °C, which is assigned to combustion of organic substances in the gel; (ii) the second weight loss of about 24% occurs in the range of 330–420 °C due to the combustion of organic substances further in the gel; (iii) the final weight



Fig. 1. TGA and SDTA curves of Mg-Ti gel.

loss of about 13% occurs between 420 and 500 °C, corresponding to the SDTA peak at 465 °C, is assigned to generation of  $Mg_2TiO_4$ solid phase, simultaneously, accompanied by some organic residue oxidation and combustion reactions which release  $CO_2$  into the air. No apparent peak and weight loss can be observed over 500 °C. All possible crystallite species generated in each step are identified by XRD measurements in Fig. 2.

#### 3.2. Crystal phases of calcined Mg–Ti gel at different temperatures

Fig. 2(a) and (b) shows the XRD patterns of all samples calcined in air at different temperatures for 2 h. As shown in Fig. 2(b), the XRD patterns of 250 and 300 °C samples are similar to that of gel sample, which indicate that the network structure of magnesium-titanium oxide polymer is destroyed gradually from room temperature to 300 °C, and it is almost destroyed completely over 350 °C. Meanwhile, there is no significant crystal phase observed between 350 and 400 °C, which indicates that some amorphous phases are initially generated. In Fig. 2(a), the trace of metastable phase Mg<sub>2</sub>TiO<sub>4</sub> (JCPDS, 25-1157) peaks can be found from XRD pattern of 450 °C. When the temperature is up to 500°C, the apparent peaks of Mg<sub>2</sub>TiO<sub>4</sub> are found. With increasing the calcination temperature, the peaks of Mg<sub>2</sub>TiO<sub>4</sub> nearly disappears at 550 °C. Simultaneously, new solid phase of MgTiO<sub>3</sub> (JCPDS, 06-0494) is generated. The peaks of MgTiO<sub>3</sub> get stronger and stronger with increasing the calcined temperature. All measured XRD patterns strongly confirm our TG/SDTA analysis for the dried gel.

#### 3.3. FTIR spectrometry

#### 3.3.1. FTIR of distillate and Mg-Ti gel

The collected distillate was analyzed by FTIR shown in Fig. 3. All absorption bands in the FTIR spectrum are in good agreement with the standard spectrum of n-butanol [19]. Hence, the above FTIR spectrum proves that n-butanol is generated during the preparation of Mg–Ti gel. Meanwhile, according to the experimental phenomena of the little bubbles generated by adding tetrabutyl titanate in the preparation of Mg–Ti gel, the possible reactions in the preparation of Mg–Ti gel can be written as follows:  $R = C_{17}H_{35}$ 

$$Ti(OC_{4}H_{9})_{4} + 4H_{2}O \rightarrow Ti(OH)_{4} + 4C_{4}H_{9}OH$$
(1)  

$$OOCR$$

$$\downarrow OOCR$$

$$\downarrow OOCR + 4H_{2}O$$

$$\downarrow OOCR + 2H_{2}O$$

$$\downarrow OOCR$$
(2)



Fig. 2. XRD patterns of Mg–Ti gel calcined at different temperatures, (a) 450–650  $^\circ$ C; (b) gel-400  $^\circ$ C.

 $RCOOH + C_4H_9OH \rightarrow RCOOC_4H_9 + H_2O$ (3)

Because the whole preparation process is in the open air, tetrabutyl titanate easily absorbs moisture from air, and then hydrolyzes to generate n-butanol. The distillate FTIR in Fig. 3 shows that reaction (1) is actually occurred. Subsequently, the melt stearic acid can



Fig. 3. FTIR spectrum of distillate collected from the Mg-Ti gel.



Fig. 4. FTIR spectrum of the Mg-Ti gel.

naturally react with the products generated by reaction (1). So the reactions (2) and (3) should be existed in the SAG system. Vice versa, the generated water in reactions (2) and (3) can promote reaction (1). That is to say, the reactions of (1) and (2) or (1) and (3) promote each other. As a result, all reactions are carried out completely in the preparation of Mg–Ti gel.

In order to confirm that the possible reactions (2) and (3) occurred in the preparation process of Mg-Ti gel, FTIR is performed to trace the organic species of Ti(IV)-stearic complexes and butyl stearate in the Mg-Ti gel. Fig. 4 shows FTIR spectrum of Mg-Ti gel. In Fig. 4, the strong peaks at 2920 and 2852 cm<sup>-1</sup> can be assigned to the symmetric and asymmetric vibrations of -CH2- and -CH<sub>3</sub> groups, respectively. The CH<sub>2</sub> scissoring and in-phase rocking bands appear at around 1462 and 719 cm<sup>-1</sup>, respectively. All these observations confirm the existence of long organic chains in the Mg-Ti gel [20]. Peaks at 1745 and 1178 cm<sup>-1</sup> represent the stretching vibration band of C=O and C-O-C groups belonging to ester, which indicate that the reaction (3) may occur to form butyl stearate in the Mg-Ti gel. According to some documents [21], the absorbance bands are attributable to the bidentate of Ti(IV)-carboxylic complexes are observed at 1550-1590 cm<sup>-1</sup> (antisymmetric) and 1430–1470 cm<sup>-1</sup> (symmetric). The latter is overlapped by the scissoring frequency of -CH<sub>2</sub>- at 1464 cm<sup>-1</sup> and, consequently, forms a broaden band. The corresponding large absorbance bands at around 1462 and 1570 cm<sup>-1</sup> in Fig. 4 indicate that the Ti(IV)-stearic complexes are formed in the Mg-Ti gel. The proposed reaction (2) occurs indeed. Therefore, the above assumption of reactions (1)-(3) occurred in the preparation of Mg-Ti gel are credible.

#### 3.3.2. FTIR of calcined samples

To trace some possibly organic species existed in the calcined gels, the FTIR spectra for the as-prepared samples at different calcination temperatures are shown in Fig. 5. The small absorption bands around 2800–3000 cm<sup>-1</sup> and 1400–1600 cm<sup>-1</sup> in the 350 °C FTIR spectrum indicate that little amount of organic substance still exists. With increasing the temperature, i.e., over 400 °C, no apparent absorption bands for organic substance can be observed, while the absorption band between 500 and 700 cm<sup>-1</sup> gets stronger and stronger, which is assigned to the formation of TiO<sub>6</sub> octahedra. In addition, a broad band centered at 3460 cm<sup>-1</sup> is corresponded to the water adsorbed on the surface of nanoparticles.

The above FTIR spectra indicate that  $MgTiO_3$  phase is generated at 550 °C, and with increasing the calcination temperature,  $MgTiO_3$ crystallites grow better and better.



Fig. 5. FTIR spectra of Mg-Ti gel calcined at different temperatures.

#### 3.4. Intermediate phase detected from Mg–Ti gel to form MgTiO<sub>3</sub>

To understand well the process of MgTiO<sub>3</sub> formation in Mg–Ti gel, some blank experiments were carried out for Mg gel and Ti gel. The phase development in Mg gel and Ti gel was characterized by XRD under the same conditions as the previous Mg–Ti gel (Figs. 6 and 7).

In Fig. 6, no MgO phase can be observed for 250 and 300 °C XRD patterns. Referring to the gel XRD pattern in Fig. 2(b), the peaks at around  $2\theta = 10^{\circ}$  and  $21^{\circ}$  can be assigned as that the Mg gel network structure is not destroyed completely. When the temperature is over 350 °C, the gel network structure is destroyed completely and MgO (JCPDS, 45-0946) phase is formed. With increasing the calcined temperature, the intensities of MgO peaks become stronger and stronger.

In Fig. 7, no apparent peaks can be observed for 300 °C XRD pattern, which indicates that the Ti gel network structure is almost destroyed completely, and all possible generated phases are amorphous. When the temperature is over 350 °C, the mixture of anatase and rutile phases is formed. Anatase is the dominant phase at low temperatures (e.g., <500 °C), while by further increasing the temperature, rutile becomes the dominant crystal phase in the calcined mixture.



Fig. 6. XRD patterns of Mg gel calcined at different temperatures.



Fig. 7. XRD patterns of Ti gel calcined at different temperatures.

From Figs. 6 and 7, it is confirmed that TiO<sub>2</sub> and MgO crystal phases can only be formed directly in their corresponding calcined stearic acid gel. In contrast with the above Ti gel and Mg gel, the only metastable phase Mg<sub>2</sub>TiO<sub>4</sub> instead of TiO<sub>2</sub> and MgO crystal phases can be detected in the calcined Mg–Ti gel by XRD, which indicates that the metastable phase Mg<sub>2</sub>TiO<sub>4</sub> is formed by excessive MgO interacting with TiO<sub>2</sub> in the calcined Mg–Ti gel. Otherwise, TiO<sub>2</sub> and MgO crystal phases should be detected by XRD in the calcined Mg–Ti gel. The possible reason is that MgO can be more easily evolved from the calcined Mg–Ti gel than that of TiO<sub>2</sub>, so excessive MgO reacts with TiO<sub>2</sub> to form the metastable phase Mg<sub>2</sub>TiO<sub>4</sub>. This evidence can be found in Figs. 6 and 7. The well-grown crystal MgO can be obtained even at 350 °C in Fig. 6, but for TiO<sub>2</sub>, the corresponding temperature to obtain well-grown crystal TiO<sub>2</sub> must be over 400 °C. The reaction can be described as follow:

$$2MgO + TiO_2 \rightarrow Mg_2TiO_4 \tag{4}$$

With increasing temperature, the rest of  $TiO_2$  is evolved from the calcined Mg–Ti gel, and then when the temperature is high enough (e.g., 550 °C), the following solid reaction may happen:

$$Mg_2TiO_4 + TiO_2 \rightarrow 2MgTiO_3$$
(5)



Fig. 8. XRD patterns of Mg–Ti gel calcined at  $550\,^\circ\text{C}$  from 5 to 120 min and then immediately quenched in the atmosphere.

Hence, new solid phase of MgTiO<sub>3</sub> is generated at 550 °C, and with increasing the temperature, the MgTiO<sub>3</sub> crystal phase grows better and better (Fig. 2).

It is well known that the final solid phase reaction product is seriously affected by calcination time at a fixed temperature point. In order to clearly show the influence of calcination time on the phase evolution of the final product MgTiO<sub>3</sub>, the typical calcination temperature of 550 °C was chosen for our experiments. We calcined the Mg–Ti gel for different calcination times. In order to maintain the existed phase structure in samples as much as possible, all calcined samples were immediately quenched in atmosphere.

The trace of the phase evolution of the final product  $MgTiO_3$  was finally detected by XRD (Fig. 8). To easily observe the corresponding crystal phases, the original XRD patterns (e.g., 5, 10, 15 and 30 min) in Fig. 8 are smoothed by the software of Origin, using the 5



Fig. 9. TEM image of  $MgTiO_3$  nanoparticles derived from Mg–Ti gel calcined at 600  $^\circ\text{C}.$ 



Fig. 10. Size distribution of MgTiO<sub>3</sub> nanoparticles.

point Adjacent Averaging Method. Fig. 8 shows that the metastable  $Mg_2TiO_4$  is the dominant phase between 5 and 30 min. When the calcined time is extended to 2 h, the metastable  $Mg_2TiO_4$  phase disappears and the  $MgTiO_3$  crystal phase becomes the dominant phase. Therefore, the metastable phase  $Mg_2TiO_4$  is also identified as the intermediate phase of  $MgTiO_3$  even at a fixed calcination temperature point.

#### 3.5. Morphology observation

Fig. 9(a) and (b) shows the transmission electron images of  $MgTiO_3$  nanoparticles prepared by calcined the Mg-Ti gel at 600 °C for 2 h. Fig. 10 shows the size distribution of the  $MgTiO_3$  nanoparticles observed from the transmission electron images. The results clearly show that  $MgTiO_3$  nanoparticles only consist of nanoscale crystallites with the average size of about 60 nm. Most  $MgTiO_3$  crystallites do not aggregate to form large particles. Nearly all crystallites are almost ellipse in shape, and well dispersed with a slight agglomeration. The mechanism of  $MgTiO_3$  formation may elucidate its small crystallite size, i.e., the phase  $Mg_2TiO_4$ , amorphous phase and  $MgTiO_3$  may affect each other and result in a low growth rate of  $MgTiO_3$  crystallites.

#### 4. Conclusions

In the present work, the phase evolution of MgTiO<sub>3</sub> from the calcined stearic acid gel in air is investigated by three kinds of

gels, such as Mg–Ti, Mg and Ti gel. In the preparation of stearic acid gel, several reactions occur to form magnesium–titanium oxide network polymer gel, meanwhile n-butanol is generated. The decomposition process of the dried Mg–Ti gel consists of a series of oxidation and combustion reactions in air, accompanied by exothermal phenomena. The metastable intermediate phase of Mg<sub>2</sub>TiO<sub>4</sub> is identified successfully for the first time. XRD measurement strongly confirms that the metastable phase Mg<sub>2</sub>TiO<sub>4</sub> can be initially formed at about 450 °C, and then react with amorphous TiO<sub>2</sub> to form MgTiO<sub>3</sub> phase. With increasing the calcination temperature, the crystallinity of the as-prepared MgTiO<sub>3</sub> nanoparticles can be improved significantly. The mechanism of the phase evolution of MgTiO<sub>3</sub> is in favor of forming nanoscale crystallites of MgTiO<sub>3</sub>.

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