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# A facile co-precipitation synthesis of hexagonal (Zn, Mg)$TiO_3$

K. He [a], R.Y. Hong [a,b,*], W.G. Feng [c], D. Badami [d]

[a] College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, SIP, Suzhou 215123, China
[b] College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, China
[c] Nanocom Inc., Suzhou 215011, China
[d] Department of Chemical Engineering, University of Waterloo, Waterloo, ON, N2L 3G1 Canada

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ABSTRACT

Dielectric zinc magnesium titanate (ZMTO) was synthesized by a facile co-precipitation method using $TiOSO_4$ as the Ti source. The decomposition and phase evolvement of the as-prepared precipitates during heat treatment were characterized by thermogravimetry analysis (TGA) and Fourier-transforming infrared (FT-IR) spectroscopy. X-ray diffractometry shows that different pH levels have a significant influence on the crystallization of the as-prepared precipitate due to the magnesium doping content. SEM images and EDS data show that fine hexagonal (Zn, Mg)$TiO_3$ powders with a Mg doping content of 2.29 at.% could be obtained at a pH of 9 and a calcination temperature of 800 °C. After sintering at 1000 °C, hexagonal (Zn, Mg)$TiO_3$ demonstrated a dielectric constant of 26–24 along with a low dielectric loss of $9.82 \times 10^{-4}$–$6.35 \times 10^{-4}$ at measurement frequencies between $10^8$ and $10^9$ Hz.

## 1. Introduction

The development of microwave dielectric materials with a good combination of a high dielectric constant (for miniaturization), a low dielectric loss (for selectivity) and a low processing temperature (for low cost and low co-fired ceramic capacitors) has been intensified so that they can be used as dielectric resonators, capacitors and filters [1,2]. Earlier, majority of the research has been focused on materials having a high dielectric constant or low loss. Only a few studies on low-temperature sinterable microwave dielectrics have been reported despite the need for applications using low-temperature sintering, such as multilayer capacitors and dielectric filters, using silver or copper electrodes, which should be sintered at below 1050 °C [3].

Zinc titanates based materials have been thoroughly investigated for applications in many fields such as paint pigment, gas sensor and catalytic sorbent [4]. However, zinc titanate was not considered as an attractive material for low-fired microwave dielectric devices until its dielectric properties were investigated by Sugiura et al. [5] at low frequency and Haga et al. [6] at microwave frequency. There are three compounds that exist in the zinc titanate system: $Zn_2TiO_4$, $ZnTiO_3$ and $Zn_2Ti_3O_8$. Hexagonal $ZnTiO_3$ is reported to have superior dielectric properties compared to the other phases. However it is unstable at high temperature and would transform into cubic ($Zn_2TiO_4$) and rutile at 945 °C [7] while it remains as a defect cubic spinel $Zn_2Ti_3O_8$ with ordered cation vacancies within the structure at low temperature [8]. The formation of $Zn_2TiO_4$ and $Zn_2Ti_3O_8$ is limited by the presence of anatase, whereas $ZnTiO_3$ is only formed in the presence of rutile [9,10]. Therefore, many efforts have been made to prepare $ZnTiO_3$ with improved stability. In previous work, divalent cations, such as $Mg^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, etc. were introduced to $ZnTiO_3$ and their thermal stability was found to be much better than that of $ZnTiO_3$ [1,11–13].

It is well known that $ZnTiO_3$ and $MgTiO_3$ have the same crystal structure of rhombohedral symmetry with a hexagonal unit cell. It is possible to substitute a zinc ion with a magnesium ion to form a (Zn, Mg)$TiO_3$ solid-solution, which might improve the thermal stability and dielectric properties [13]. Kim et al. [1] and Hsieh et al. [14] reported that the $(Zn_{1-x}Mg_x)TiO_3$ solid-solution has improved thermal stability and dielectric properties. The thermal stability region of $ZnTiO_3$ could be extended at a rate of ~10 °C per 1 mol% of magnesium substitution in this composition range and thus when $x = 0.2$ the decomposition temperature of hexagonal phase to cubic and rutile phase was increased up to ~1100 °C.

Recent researches mainly focus on the preparation of zinc titanates by solid-state and sol–gel methods. Many researchers have reported their works on the solid-state reaction of ZnO–MgO–$TiO_2$ solid-solution [15–17]. Although they were successful in the preparation of zinc magnesium titanate from stoichiometric raw materials such as ZnO, MgO/$MgCO_3$ and $TiO_2$, the reaction process is cumbersome, suffering from chemical inhomogeneity and usually takes more than 12 h of high energy ball milling which is a costly process. Nanometer scale $ZnTiO_3$ powders can be successfully synthesized by sol–gel methods [18,19,20], semi-chemical synthesis [1] and chemical bath deposition [21]. However, these processes are too complex and

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[*] Corresponding author at: College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, SIP, Suzhou 215123, China. Tel./fax: +86 512 6588 2057.
*E-mail address:* rhong@suda.edu.cn (R.Y. Hong).

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the raw materials are too expensive to reach an industrial production level.

In the present work, a co-precipitation method was used to fabricate the (Zn, Mg)$TiO_3$ at the nano-scale level. The Ti source $TiOSO_4$ is relatively inexpensive as it is a by-product from the $TiO_2$ industry [22]. Many researches have already reported the synthesis of nanosized $TiO_2$ from $TiOSO_4$ [23,24], but there is no research focus on the synthesis of zinc titanates from $TiOSO_4$ using co-precipitation methods. It is important to control the pH of the metal containing solution and the calcination temperature to find the optimum condition for the hexagonal (Zn, Mg)$TiO_3$ products. The thermal and crystallization behavior of ZMTO products was studied. In order to obtain the hexagonal (Zn, Mg)$TiO_3$ products, the effects of pH and calcination temperature on the crystal structures and dielectric properties were studied in detail.

## 2. Experimental procedure

### 2.1. Materials

Zinc sulfate heptahydrate ($ZnSO_4\cdot 7H_2O$, AR), magnesium sulfate anhydrous ($MgSO_4$, AR), aqueous ammonia ($NH_3\cdot H_2O$, 25–28 wt.%, AR) and anhydrous ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification. The industrial grade $TiOSO_4$ (97%) was used as the $Ti^{4+}$ source.

### 2.2. Sample preparation

(Zn, Mg)$TiO_3$ samples were prepared using a simple co-precipitation method. The 0.5 M $TiOSO_4$ solution was obtained firstly by dissolving $TiOSO_4$ powders in a 0.5 M $H_2SO_4$ solution and then by filtering the insoluble substance. Then 0.04 mol $ZnSO_4\cdot H_2O$ and 0.01 mol $MgSO_4$ were dissolved in 100 ml $TiOSO_4$ solution to ensure the molar concentration of 0.4 M $Zn^{2+}$, 0.1 M $Mg^{2+}$ and 0.5 M $Ti^{4+}$ according to $Zn_{0.8}Mg_{0.2}TiO_3$ [15]. The mixed solution is put into a four neck flask. Precipitation reagent of 5 M ammonia solution was dropped quickly into the flask with vigorous stirring in a water bath with sonification and the pH was kept constant at 7, 8, and 9. The reaction lasted 2.5 h and after several hours of aging, the precipitate was washed with deionized water and alcohol several times. The resultant slurry was then dried and calcined at 600–900 °C for 3–4 h. The calcined powders were grounded to fine powders, then granulated using a 2 wt.% polyvinyl alcohol (PVA, mw 1750) solution and pressed into cylindrical disks of about 10 mm diameter and 2–3 mm thickness by applying a pressure of about 20 MPa. These compacts were covered by powders of the same composition and sintered at a temperature of 1000 °C for 4 h.

### 2.3. Characterization

The decomposition of the precursors during heat treatment was characterized by thermogravimetry analysis (TGA) on a PerkinElmer Pyris 1 instrument under $N_2$ atmosphere in the temperature range of 20–800 °C with a heating rate of 10 °C/min. Fourier-transform infrared (FT-IR) spectroscopy was carried out using the potassium bromide (KBr) disk method by a Nicolet Avatar 360 Fourier transform infrared spectrometer. The crystalline structure and phase purity of ZMTO samples were identified by a Panalytical X'Pert-Pro MPD X-ray diffraction (XRD) using Cu-Kα radiation ($\lambda = 1.5406$ Å) in the scanning range 2θ between 20° and 80°. The microstructures of the calcined and sintered samples were studied using a Hitachi S-4700 scanning electron microscope (SEM) attached with Energy Dispersive Spectroscopy (EDS) to determine the surface elemental composition. Densities of all the sintered samples were measured using the Archimedes technique. The microwave dielectric properties were measured in the frequency range of $10^8$–$10^9$ Hz using a Novocontrol Broadband Dielectric impedance spectrometer with a HP4191 network analyzer.

## 3. Result and discussion

### 3.1. Co-precipitation process

According to Ahmed et al. [25], the $TiOSO_4$ solution contains chains of Ti and O atoms which are interconnected by $SO_4^{2-}$ groups. The $-Ti^{2+}-O-Ti^{2+}-O-$ zigzag chains or oligomers have different chain lengths based on the $TiOSO_4$ concentration. At a low concentration, it has been showed that monomeric titanyl species with 2+ charge, as well as dimers or trimmers are present. However, the number of monomeric titanyl decreases as the concentration of $TiOSO_4$ increases. At high concentrations of titanyl, the percentage of monomeric form is negligible and titanium is mainly in the zigzag chains of $-Ti^{2+}-O-Ti^{2+}-O-$. Under hydrolysis condition OH groups attach to these chains. The solubility of partially hydrolyzed $-Ti^{2+}-O-Ti^{2+}-O-$ chains is less than that of their precursors. Then these particles agglomerate to the secondary and tertiary particles of titania. The primary $3TiO_2\cdot 4H_2O$ particles are produced in non-equilibrium conditions (high oversaturation, quick hydrolysis) and do not have a pronounced crystal shape. In the dilute $TiOSO_4$ solutions, titanyl ions are present mainly in monomeric form. Hydrolysis of the monomeric form results in the $TiO(OH)_2$-hydrolyzed monomeric form and the slow growth of $3TiO_2\cdot 4H_2O$ particles occurs from the diluted $TiO(OH)_2$ solution. These two mechanisms of the $TiO_2$ formation from the $TiOSO_4$ solution are known as crystal-chemical and colloidal chemical mechanism. Obviously, the high initial concentration of $TiOSO_4$ results in a loose structure of the secondary particles and thus there is a large available surface for the co-crystallization with $(Zn_{1-x}Mg_x)(OH)_2$ precipitates.

The following Eqs. (1) and (2) describe the co-precipitation process [23,26]:

$$(1-x)ZnSO_4 + xMgSO_4 + 2NH_3\cdot H_2O \rightarrow \left(Zn_{(1-x)}Mg_x\right)(OH)_2\downarrow + (NH_4)_2SO_2 \quad (1)$$

$$\left(-Ti^{2+}-O-Ti^{2+}-O-\right)_n + 4nOH^- \rightarrow \left[-Ti(OH)_2-O-Ti(OH)_2-O-\right]_n \rightarrow 2/3n[3TiO_2\cdot 4H_2O]\downarrow. \quad (2)$$

In the solid-state reaction, the formation and transformation of $ZnO–TiO_2$ system are formed as follows [16,17,27]:

$$ZnO + TiO_2 \xrightarrow{\Delta(\sim 700\,^{\circ}C)} ZnTiO_3 + Zn_2Ti_3O_8 \quad (3)$$

$$Zn_2Ti_3O_8 \xrightarrow{\Delta(\sim 820\,^{\circ}C)} ZnTiO_3 + TiO_2 \quad (4)$$

$$ZnTiO_3 + Zn_2Ti_3O_8 \xrightarrow{\Delta(\sim 945\,^{\circ}C)} Zn_2TiO_4 + TiO_2. \quad (5)$$

During the co-precipitation, the influence of Mg doping, the crystal formation and transformation is complicated. The heating process could be assumed as follows:

$$(b+d)/3(3TiO_2\cdot 4H_2O) + a\left(Zn_{(1-x)}Mg_x\right)(OH)2 \xrightarrow{\Delta(>600\,^{\circ}C)} \left(Zn_{(1-x)}Mg_x\right)_a Ti_bO_c + dTiO_2. \quad (6)$$