Preparation and Characterizations of ZnTiO$_3$ Powders by Sol–Gel Process

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Abstract. ZnTiO$_3$ powders were prepared by a sol–gel method. The gelation conditions and the gelation mechanism were investigated. The crystallization behavior and characteristics of the ZnTiO$_3$ were also investigated in detail. The experimental results show that homogenous and translucent gels can be prepared when the gelation conditions are appropriate and the gelation temperature remains constant. The gel structure can be described as a network of Ti and O, in which zinc ions are well distributed. The ZnTiO$_3$ phase can be detected by XRD in the powders calcined above 700$^\circ$C. The formation of ZnTiO$_3$ is a slow reaction process, which leads to the development of large ZnTiO$_3$ particles, with dimensions after calcination at 900$^\circ$C for 2 h in the range of 30–50 $\mu$m.

Keywords: zinc titanate, sol–gel, crystallization behavior, characteristic

1. Introduction

The demand for the development of dielectric materials for microwave frequencies is increasing with the rapid progress in mobile and satellite communication systems. High performance with low loss and stable resonance-frequency temperature-coefficient is the basic requirement of dielectric resonators and filters [1, 2]. ZnTiO$_3$-based ceramics are promising dielectric materials for temperature-stable capacitors or microwave devices due to their low loss at high frequency [3]. ZnTiO$_3$ is also a useful candidate for gas sensors [4] (for ethanol, NO, CO, etc.), catalysts [5] and paint pigments [6].

The pure ZnTiO$_3$ phase cannot be prepared from an equimolar mixture of ZnO and TiO$_2$ because the compound decomposes into Zn$_2$TiO$_4$ and rutile at –945$^\circ$C [7]. The partial substitution of zinc with divalent cations (e.g. Sr, Ba, Ni, and Mg) could provide enhanced temperature stability as well as dielectric properties [8]. However, for studying the effect of synthesis method on the ZnTiO$_3$ crystallization, it is still meaningful to investigate undoped samples.

ZnTiO$_3$ is mainly prepared by the solid-state reaction method [7, 8]. Only a few studies have reported the preparation of ZnTiO$_3$ by sol–gel processing [9, 10]. Usually, the crystallization temperature of ZnTiO$_3$ in the sol–gel process is lower than that in the solid-state reaction route. This suggests the possibility of preparing ZnTiO$_3$-based ceramics at a low temperature via sol–gel processing. In this paper, the authors have synthesized ZnTiO$_3$ powders in a simple system by a sol–gel method and investigate the gelation mechanism, crystallization behavior of ZnTiO$_3$ and the characteristics of the powders obtained.

2. Experimental Details

The sol–gel procedure used to prepare ZnTiO$_3$ powders is illustrated in Fig. 1. The precursor solution was prepared from analytical grade Zn(CH$_3$COO)$_2$·2H$_2$O and Ti(OC$_2$H$_5$)$_4$ to achieve a Zn:Ti mole ratio of 1. A mixture of CH$_3$COOH and Ti(OC$_2$H$_5$)$_4$ was added to an aqueous solution of Zn(CH$_3$COO)$_2$·2H$_2$O ([Zn(CH$_3$COO)$_2$·2H$_2$O] = 3.7 M; H$_2$O:Ti mole ratio = 45, 50, 55, 60, 63 or 70; H$_2$O:CH$_3$COOH volume ratio = 1, 1.3, 1.5, 1.7 or 1.9) with stirring and heating at about 50$^\circ$C. A transparent sol was obtained, which formed a gel over a period of several hours. The
resulting sol–gel precursor powders were calcined at 500–900°C for 2 h to obtain the final powders.

Thermal analysis of dry gel powders was performed by thermogravimetric and differential thermal analysis (TG-DTA, SDT2960, America). Phase structure identification of the calcined powders was performed by X-ray diffraction (XRD, Dmax-3c, Rigaku, Japan) using Cu Kα radiation and a graphite monochromator. The microstructure was examined by scanning electron microscopy (SEM, JSM-5600, Jeol, Japan). Energy dispersive spectroscopy (EDS, ISIS, OXFORD, U.K.) analysis was conducted on Au-coated powders specimen. The structure of particles was analyzed by micro-electron-beam diffraction linked to transmission electron microscopy (TEM, JEM-200CX, Jeol, Japan).

3. Results and Discussion

3.1. The Gelation Conditions and Gelation Mechanism

Figures 2 and 3 show the effect of gelation conditions on the gels obtained. It is evident that \(55 \leq n_{H_2O} : n_{Ti} \leq 63\) and \(V_{H_2O} : V_{HAc} = 1.5\) are the appropriate processing conditions for producing a homogenous gel. Salting-out (of a zinc-containing compound) usually occurred in a system with decreasing water volume or increasing acetic acid volume. In contrast, the color of the gel became gradually white with increasing water volume or decreasing acetic acid volume, because these conditions promote the hydrolysis of Ti(OC\(_4\)H\(_9\))\(_4\).

During the gel aging process, it was found that maintaining a constant temperature is very important for obtaining a transparent and homogenous gel. The gel usually became whiter and more opaque when the aging temperature increased. When the aging temperature decreased, the homogenous gel was usually destroyed by the salting-out or the seepage of a small amount of liquid phase.

The formation of the gel is due to the hydrolysis of Ti(OC\(_4\)H\(_9\))\(_4\), which can be described by:

\[
\text{Ti}(\text{OC}_4\text{H}{}_{9})_4 + x\text{H}_2\text{O} \rightarrow \text{Ti}(\text{OC}_4\text{H}{}_{9})_4-x(\text{OH})_x + x\text{C}_4\text{H}_9\text{OH},
\]

and other similar reactions.

In the homogenous gel (i.e. in the absence of salting out of Zn-containing phases) it can be inferred that zinc ions are well distributed in the Ti-O network.

3.2. Crystallization Behavior of Zinc Titanate

The dry gel powders were analyzed for burnout behaviors by TG-DTA. Figure 4 shows TG-DTA curves of the gel powders heated in flowing air at 20°C/min. The TG curve indicates that there is an initial weight loss of 4.6% followed by another 47.5% weight loss. They take place (1) below 150°C and (2) between 150°C and

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\text{Heated at 50°C}
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Maintained 50°C for several hours

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\text{Calcining at different temperature}
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\text{Powders for XRD, SEM, EDS, TEM}
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