

Formation and transformation of ZnTiO_3 prepared by sol–gel process

Lei Hou, Yu-Dong Hou, Man-Kang Zhu*, Jianlan Tang, Jing-Bing Liu, Hao Wang, Hui Yan

The Key Laboratory of Advanced Functional Materials of China Education Ministry, Beijing University of Technology, Beijing 100022, China

Received 22 April 2004; received in revised form 8 July 2004; accepted 10 July 2004

Available online 14 October 2004

Abstract

ZnTiO_3 powders with pure hexagonal phase were prepared by the sol–gel process with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ materials. The thermal behavior and phase transformation of the gels were investigated by the differential scanning calorimetry–thermogravimetry (DSC–TG) analysis, X-ray diffraction (XRD) patterns, Fourier-transforming infrared (FT-IR) spectroscopy, and Raman scattering spectroscopy. The results revealed that pure hexagonal phase of ZnTiO_3 could be obtained at low temperature of 800 °C. However, in further increased temperature above 900 °C, hexagonal ZnTiO_3 would decompose into cubic Zn_2TiO_4 and rutile TiO_2 .

© 2004 Elsevier B.V. All rights reserved.

Keywords: Sol–gel process; Ceramic; ZnTiO_3 ; Structure analysis

1. Introduction

With the recent progress of microwave applications, including mobile telephones and satellite communication system, the development of high-quality microwave dielectrics has been intensified so that they can be used as dielectric resonators, capacitors, and filters. Zinc titanates are promising candidates as dielectric materials for microwave devices and more preferably for low-temperature cofired ceramics (LTCCs) [1–3]. It is reported that three compounds exist in the ZnO–TiO_2 system, including Zn_2TiO_4 (cubic), ZnTiO_3 (hexagonal), and $\text{Zn}_2\text{Ti}_3\text{O}_8$ (cubic) [4–6]. Among these compounds, ilmenite-type hexagonal ZnTiO_3 -based ceramic has been reported to have superior electrical properties: a dielectric constant ϵ_r of 19, $Q=3000$ (at 10GHz), and $\tau_f=-55$ ppm/°C, which is very similar to those of other ilmenite-type titanates [3,7,8]. Many efforts have been made to prepare pure ZnTiO_3 powders and ceramics. Although Zn_2TiO_4 can easily be prepared by conventional solid state reaction between 2ZnO and 1TiO_2 [9], the preparation of pure ZnTiO_3 from a mixture of 1ZnO

and 1TiO_2 was not successful. The solid state reaction method has some drawbacks of high temperature, long range of diffusion distance, large particle size, and limited degree of chemical homogeneity, resulting in difficulties to synthesize pure ZnTiO_3 powders by this method.

Sol–gel process has been successfully used in the past 2 decades for preparation of ceramics, glasses, fibers, and thin films and has shown considerable advantages over conventional solid state reaction [10–13]. These advantages include excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and lower crystallization temperature. In this paper, we present preparation and characterization of sol–gel-derived ZnTiO_3 powders. It is found that the amorphous gel can be transformed into pure ilmenite-type ZnTiO_3 through calcination at 800 °C. But the single phase of ZnTiO_3 can only exist in a narrow temperature range, and, as the temperature further increased above 900 °C, the pure ZnTiO_3 phase would decompose into Zn_2TiO_4 and rutile TiO_2 .

2. Experimental

Precursor solutions for ZnTiO_3 were prepared by the following method. Firstly, certain amounts of Zn

* Corresponding author. Tel.: +86 10 67392733; fax: +86 10 67392412.

E-mail address: zhumk@bjut.edu.cn (M.-K. Zhu).

$(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ with stoichiometry ($\text{Zn}/\text{Ti}=1:1$) were dissolved into ethanol, stirred, and refluxed for 3 h. The acetic acid was dropped into mixed solution to modulate the pH value to 1–2, and transparent sol with the pale yellow color was obtained. The sol was then heated to 80 °C slowly and dried, and, finally, a brown puffy porous gel was obtained.

Differential scanning calorimetry–thermogravimetry (DSC–TG) analysis was conducted by a Netzsch 439C thermoanalyser in air atmosphere over the temperature region 25–1100 °C at a heating rate of 15 °C min^{-1} . The X-ray diffraction (XRD) patterns were recorded by Bruker 8D advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation. A step scan with a step size of 0.02° was used with a counting time of 1 s/step. The Fourier-transforming infrared (FT-IR) spectroscopy was performed on dispersion in potassium bromide using the pressed-disk method by Xiantek FT-IR spectrometer in the range from 400 to 2000 cm^{-1} . Raman spectra were carried out using an established Raman back-scattering setup with a resolution of 2 cm^{-1} .

3. Results and discussion

In this work, differential scanning calorimeter (DSC) analysis was used to analyse the crystallization process of as-prepared gels. Combined with thermogravimeter (TG) analysis, the heat process of a material with increasing temperature can be determined. Fig. 1 shows the DSC–TG curve of ZnTiO_3 gel. As seen in Fig. 1, the TG curve can be divided into three main weight loss stages. The first weight loss below 300 °C can be attributed to the evaporation of solvents, such as water and alcohol, and the combustion of organic residues, corresponding to an endothermic peak at 80–120 °C and exothermic peak at 150–260 °C in DSC curve, respectively. The second step that occurs in the temperature range 300–700 °C results from the dehydroxylation of Ti-OH into TiO_2 and decomposition of the NO_3 group, as corroborated by significant exothermic peaks

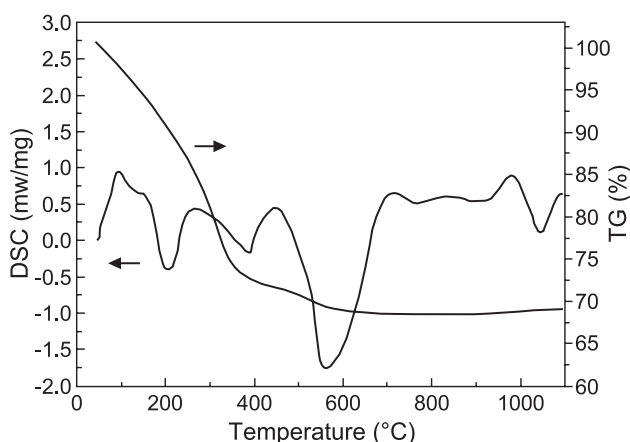


Fig. 1. The DSC and TG curves of ZnTiO_3 gel.

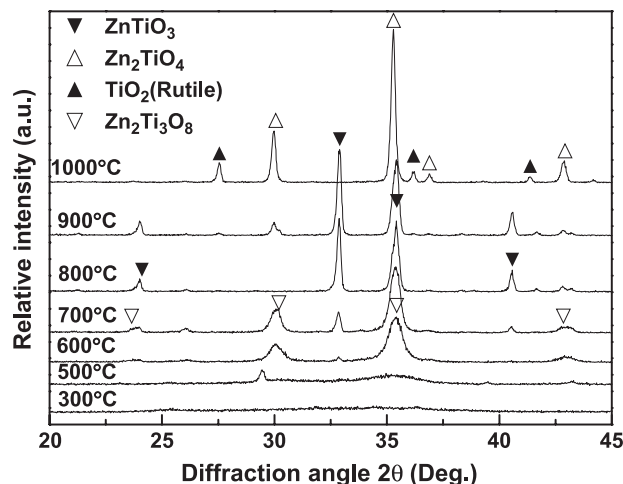


Fig. 2. XRD patterns of powders calcined at different temperatures.

appeared at 350–450 and 500–650 °C in DSC curve, respectively [11]. In the final step over 700 °C, little of weight loss can be observed, but an endothermic peak appears at about 900–1000 °C in DSC curve, which indicates that the phase transformation of ZnTiO_3 occurred, as revealed by the later XRD patterns.

On the basis of DSC–TG analysis, the gel powders were heat-treated between 500 and 1000 °C for 3 h in air. Fig. 2 shows the XRD patterns of the gel and those calcined at

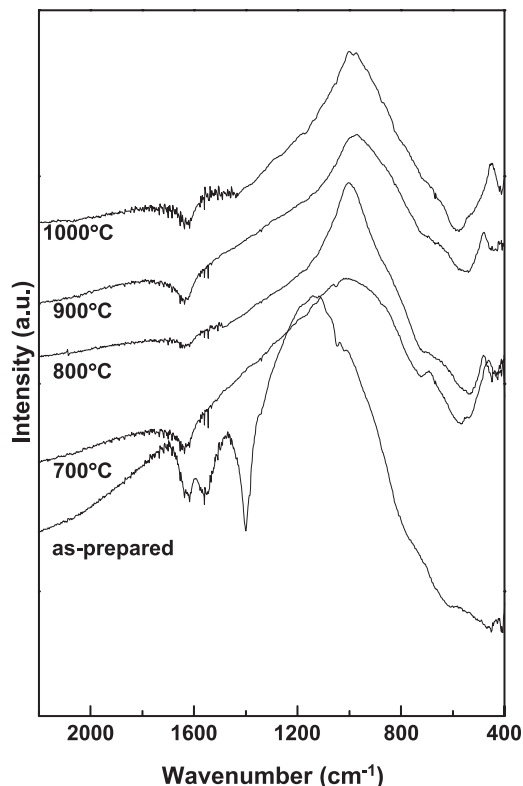


Fig. 3. Infrared spectra of powders calcined at different temperatures.

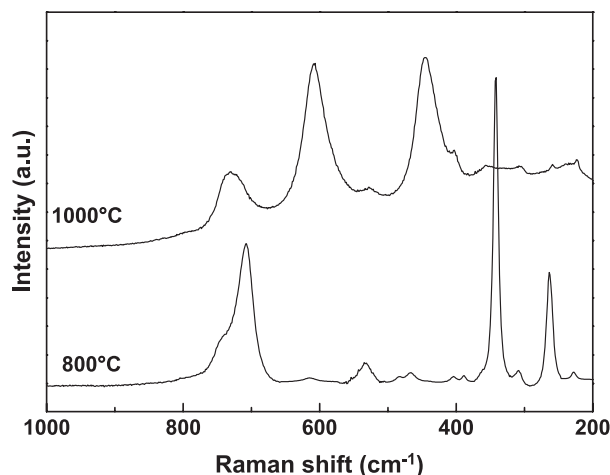


Fig. 4. Raman spectra of powders calcined at different temperatures.

500, 600, 700, 800, 900, and 1000 °C, respectively. It can be seen that the starting powders were amorphous, and no significant change in structure up to the temperature of 500 °C was observed, which means that no crystallization happened in the gel. At 600 °C, some peaks appeared, and the intensity increased rapidly up to 700 °C. The crystalline phase was identified to be cubic $Zn_2Ti_3O_8$, which is a low-temperature form of ZnO–TiO₂ system, as reported by Yamaguchi et al. [14]. It should be given more attention that, when the temperature further rises up to 800 °C, except for the hexagonal form of ilmenite $ZnTiO_3$, no other compounds and free species were observed. This result indicated that the transformation of cubic $Zn_2Ti_3O_8$ to hexagonal $ZnTiO_3$ was complete, although no significant DSC peak was detected. Wang et al. reported the preparation and characterization of sol–gel-derived $ZnTiO_3$ crystals, but they only acquired cubic $ZnTiO_3$, and no pure hexagonal $ZnTiO_3$ has been obtained [15]. The difference from our results may come from the different sol–gel process. However, when the temperature increased above 900 °C, the peaks of rutile TiO₂ and cubic Zn_2TiO_4 were observed, which resulted from the decomposition of hexagonal $ZnTiO_3$, corresponding to the endothermic peak at about 900–1000 °C in the DSC curve, as seen in Fig. 1.

Fig. 3 shows the FT-IR spectra of samples calcined at different temperatures. For the as-prepared gel, the broad band at 1630 cm^{-1} is attributed to absorbed water. The peaks at about 1560 and 1395 cm^{-1} are due to the N–O bond vibration of NO_3^- and carboxyl vibration, respectively. Generally, the bands in the low-wave number region (400–650 cm^{-1}) are assigned to Ti–O bond vibrations [16]. As the temperature rise above 700 °C, the absorption bands of Ti–O octahedra appeared at 590 and 560 cm^{-1} . Due to TiO₆ group existing in all forms of $ZnTiO_3$, $Zn_2Ti_3O_8$, and Zn_2TiO_4 , the IR spectra of specimens calcined between 700 and 1000 °C shows alike pattern. To further investigate the phase transformation, Raman spectra were conducted. Fig. 4 shows Raman spectra of as-prepared gels calcined at 800

and 1000 °C. It can be clearly seen that both specimens show different patterns. For the specimen heat-treated at 800 °C, the peaks located at around 703, 530, 341, and 263 cm^{-1} are attributed to the vibration modes of $\nu_1(LO)$, $\nu_1(TO)$, $\nu_2(LO, TO)$, and $\nu_4(LO)$, respectively [17], which are the characteristic peaks of hexagonal $ZnTiO_3$. However, for the specimen treated at 1000 °C, the strong Raman peaks appeared at around 445, 608, and 728 cm^{-1} . The former two peaks are characterized as E_g and A_{1g} modes of rutile TiO₂ [18], and the latter is characterized as A_{1g} mode of cubic Zn_2TiO_4 [19]. The above results are in good agreement with the thermal behavior and XRD analysis mentioned above.

4. Conclusions

The ilmenite $ZnTiO_3$ has been obtained using sol–gel method. At low temperature of 600 °C, cubic phase $Zn_2Ti_3O_8$ appeared, and, with the increasing heat-treated temperature, a cubic to hexagonal transformation occurs in the process. Complete crystallization of hexagonal $ZnTiO_3$ is obtained at about 800 °C. However, the pure hexagonal phase can only exist in a narrow temperature region; as temperature exceed over 900 °C, the ilmenite $ZnTiO_3$ would decompose into cubic Zn_2TiO_4 and rutile TiO₂.

Acknowledgement

The authors are very grateful to the part financial support of The Science and Technological Development Program of Beijing Education Committee.

References

- [1] K. Haga, T. Ishii, J. Mashiyama, T. Ikeda, Japanese Journal of Applied Physics 31 (1992) 3156–3159.
- [2] H.T. Kim, J.D. Byun, Y. Kim, Materials Research Bulletin 33 (1998) 963–973.
- [3] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Journal of the American Ceramic Society 82 (1999) 3043–3048.
- [4] F.H. Dulin, D.E. Rase, Journal of the American Ceramic Society 43 (1960) 125–131.
- [5] Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, S. Wu, T.H. Fang, Journal of Alloys and Compounds 354 (2003) 303–309.
- [6] H.T. Kim, S. Nahm, J.D. Byun, Y. Kim, Journal of the American Ceramic Society 82 (1999) 3476–3480.
- [7] A. Golovchanski, H.T. Kim, Y.H. Kim, Journal of the Korean Physical Society 32 (1998) S1167–S1169.
- [8] J.H. Sohn, Y. Inaguma, S.O. Yoon, M. Itoh, T. Nakamura, S.J. Yoon, H.J. Kim, Japanese Journal of Applied Physics 33 (1994) 5466–5470.
- [9] H.T. Kim, Y. Kim, M. Valant, D. Suvorov, Journal of the American Ceramic Society 84 (2001) 1081–1086.
- [10] X.H. Zeng, Y.Y. Liu, X.Y. Wang, W.C. Yin, L. Wang, H.X. Guo, Materials Chemistry and Physics 77 (2002) 209–214.
- [11] X.W. Wang, Z.Y. Zhang, S.X. Zhou, Materials Science & Engineering. B, Solid-State Materials for Advanced Technology 86 (2001) 29–33.
- [12] Z. Surowiak, M.F. Kupriyanov, D. Czekaj, Journal of the European Ceramic Society 21 (2001) 1377–1381.

- [13] H.Q. Fan, H.E. Kim, *Japanese Journal of Applied Physics* 41 (2002) 6768–6772.
- [14] O. Yamaguchi, M. Morimi, H. Kawabata, K. Shimizu, *Journal of the American Ceramic Society* 70 (1987) C-97–C-98.
- [15] S.F. Wang, F. Gu, M.K. Lü, C.F. Song, S.W. Liu, D. Xu, D.R. Yuan, *Materials Research Bulletin* 38 (2003) 1283–1288.
- [16] J.T. Last, *Physical Review* 105 (1957) 1740–1750.
- [17] C.H. Perry, D.B. Hall, *Physical Review Letters* 15 (1965) 700–702.
- [18] Y.H. Zhang, C.K. Chan, J.F. Porter, W. Guo, *Journal of Materials Research* 13 (1998) 2602–2609.
- [19] Z.W. Wang, S.K. Saxena, C.S. Zha, *Physical Review. B* 66 (2002) 1024103.