

Trade Science Inc.

ISSN : 0974 - 7443

Volume 6 Issue 1

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 6(1) 2011 [41-44]

Preparation of BaTiO₃-based ceramic with core-shell structure used for high-stability capacitor

Jing Wang^{1,2*}, Lan-Fen Li¹, Dan Jiang¹

¹College of Chemical and Environmental Science, HeBei University, Baoding 071002, (CHINA)

²Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, (CHINA)

E-mail : wangjing9804@163.com

Received: 8th November, 2010 ; Accepted: 18th November, 2010

ABSTRACT

The effects of Na_{0.5}Bi_{0.5}TiO₃ addition on the microstructure and dielectric properties of Zr-modified BaTiO₃ were investigated. The sintering temperature of Zr-doped BaTiO₃ could be reduced to 1100 °C by adding Na_{0.5}Bi_{0.5}TiO₃. SEM results show a core-shell structure with Na_{0.5}Bi_{0.5}TiO₃ addition. Meanwhile, DSC curves which have two curie points when the samples were added with Na_{0.5}Bi_{0.5}TiO₃ also confirmed that there were two phases existing with a core-shell structure in the samples. The permittivity decreased and the Curie temperature shifted to higher temperature when the Na_{0.5}Bi_{0.5}TiO₃ content increased. The BaTiO₃-based system shows great potential for applications in EIA X8R-type capacitors.

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KEYWORDS

BaTiO₃;
Ceramic;
Liquid-method;
High-stability capacitor;
Core-shell structure.

INTRODUCTION

Barium titanate (BaTiO₃) has been widespread used in the electronics industry because of its high dielectric constant, and piezoelectric and ferroelectric properties. The high dielectric constant of BaTiO₃ and the ease with which its electrical properties can be modified by combination with other materials make it exceptionally suitable for miniature capacitor. Because of the large variation of its dielectric properties with temperature and voltage, BaTiO₃ is not, except in rare instances, used as a dielectric without modification. Modified BaTiO₃ can be produced with a wide variation in dielectric properties. Presently, with the rapid development of automotive industry, application of capacitor, especially for those used in the engine electronic con-

trol unit (ECU), programmed fuel injection (PGMFI), and anti-lock brake system (ABS), et al., requires preferable temperature characteristics. There is increasing need to extend the working range of these devices to 150°C to achieve X8R specification (the capacitance in the temperature range of -55 to 150°C is within ±15% of room temperature capacitance)^[1]. This requires appropriate chemical doping to increase T_c. Recently, Na_{0.5}Bi_{0.5}TiO₃ (NBT) with a perovskite structure and a relatively high T_c (320°C) has been used to raise the T_c of BaTiO₃^[2]. However, Bi₂O₃ is easy to volatilize and has low capacitance at room temperature, Zr-doped BaTiO₃ growing on the surface of NBT can effectively restrain its volatilization and enhance the capacitance at room temperature.

The traditional solid state reaction is usually per-

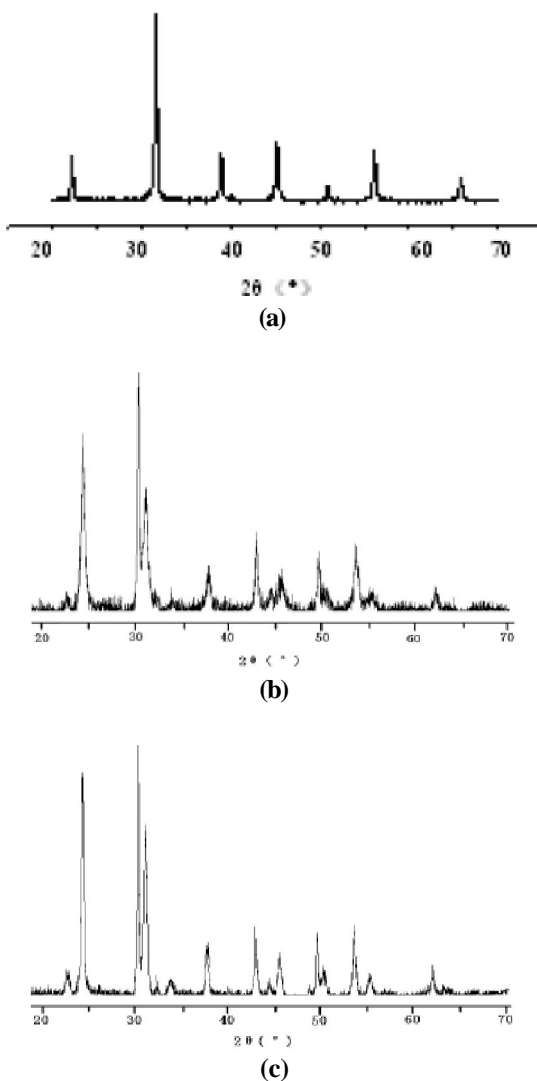


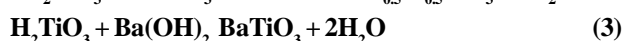
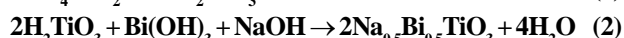
Figure 1 : XRD patterns of (a) BaTi_{0.9}Zr_{0.1}O₃, (b) 5%NBT-BaTi_{0.9}Zr_{0.1}O₃ and (c) 10%NBT-BaTi_{0.9}Zr_{0.1}O₃

formed at elevated temperature, easily leading to by-products and structural inhomogeneity. To some extent, such disadvantages impose limitations on the application and properties of the materials. In this paper, the influence of NBT on the microstructure and dielectric properties of 1% Zr-doped BaTiO₃ is investigated. The variation of T_C is used to estimate the application of the investigated ceramic material in X8R-type capacitor.

EXPERIMENTAL

The BaTiO₃-based samples studied were prepared by two steps in the following way. Firstly, NBT was prepared by microwave method with NaOH, Bi(NO₃)₃

and TiCl₄. The stoichiometric solutions were mixed in a microwave oven for 30 min at 100°C. Secondly, Ba(OH)₂, ZrOCl₂ and TiCl₄ which had mixed together was mixed with various amounts of NBT (5 and 10 mol%). The mixtures were homogenized by a magnetic stirrer placed on an electric hot plate to react below 100°C for 3 h. The solid powder of BaTiO₃-based samples were obtained after filtering, washing and drying at 100°C^[3,4]. The reaction may be described by the following formulations. The mixtures were uniaxially pressed into discs under 10MPa. Sintering was conducted at 1100°C for 1 h under ambient atmosphere.



Crystal structure of the samples were identified at room temperature using an X-ray diffractometer (XRD; Model: D-MAX IIIV, Rigaku Co., Tokyo, Japan) with Cu K α radiation, operated at 30 kV, 20mV, and a scanning rate of 1° min⁻¹ within the range of 2 θ from 20° to 70°. The lattice constants of samples were determined with the aid of silicon standard. Scanning electron micrographs (SEM) was recorded with a Jeol 940A electron microscope. Differential scanning calorimetry (DSC; Modal: DSC131, Setaram, France) was used to determine the T_c of the samples.

In order to measure the sample's electrical properties, silver electrodes were attached to the surface of the sintered discs and fired at 550°C for 30 min. Dielectric permittivity and the dissipation factor of the disc-type capacitors were measured using a LCR meter in a temperature range of -55 to 150°C at 10 kHz, 1 KHz and 100 Hz respectively.

RESULTS AND DISCUSSION

Figure 1 showed the X-ray diffraction patterns of BaTi_{0.9}Zr_{0.1}O₃, 5% NBT-BaTi_{0.9}Zr_{0.1}O₃ and 10% NBT-BaTi_{0.9}Zr_{0.1}O₃. The BaTi_{0.9}Zr_{0.1}O₃ sample showed a clear provskite phase. However, a second phase, identified as provskite-type NBT, was detected in 5% NBT-BaTi_{0.9}Zr_{0.1}O₃ and 10% NBT-BaTi_{0.9}Zr_{0.1}O₃ samples. Because the radius of Bi³⁺ (0.108 nm) and Na⁺ (0.95 nm) are all little than Ba²⁺ (0.135 nm), the pattern corresponding to NBT relatively moved rightward, which is consistent with the Bragg's law.

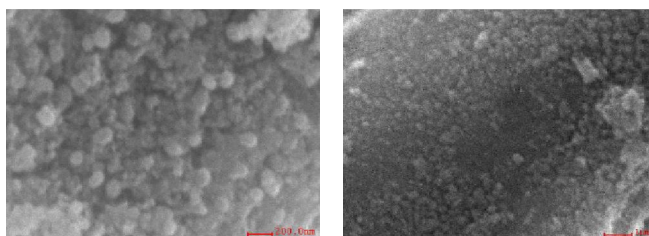


Figure 2 : SEM photos of (a) 5%NBT- $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and (b) 10%NBT- $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$

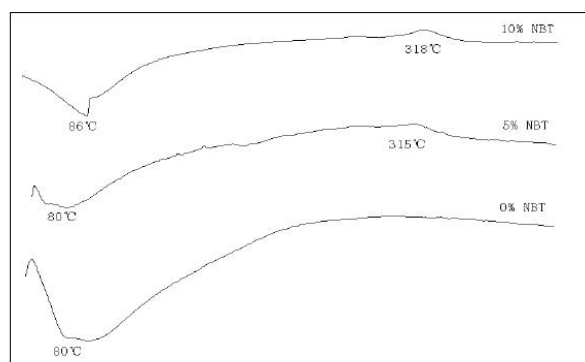


Figure 3 : Differential scanning calorimetry (DSC) curves of $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ specimens with various amounts of NBT content for the measurement of Curie temperature

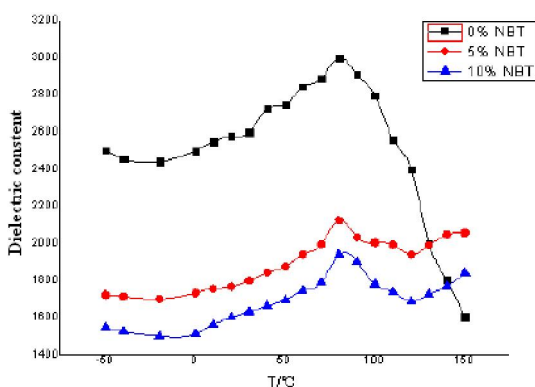


Figure 4 : Temperature dependence of dielectric constant of $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ specimens with various amounts of NBT content

Figure 2 showed the SEM micrographs of 5%NBT- $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and 10%NBT- $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$. The grain size was significantly increased from 100 nm to more than 200 nm. For both of the two samples, the SEM photographs indicated no evidence of any other phases, although the provskite-type NBT was detected by XRD. It indicated that the NBT was enclosed in the $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ phase to a core-shell structure, so that it was very difficult to detect it by SEM.

Figure 3 showed the DSC curves of $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$

with various amounts of NBT content. When there was no NBT added, the T_c of $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ is 80°C. Once NBT was added in the samples, another T_c could be detected at about 320°C. Again, the more T_c is due to the formation of core-shell structure. When the added NBT content increased from 5% to 10%, the T_c of samples at high temperature increased from 315°C to 318°C, and that at low temperature increased from 80°C to 86°C. It implied that more NBT promote the diffusion between $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ and NBT, leading to chemically inhomogeneous adulteration, which could diffuse the curie peaks and enhance the temperature stability.

Figure 4 showed the temperature dependence of the dielectric constants of the NBT- $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ system for various amounts of NBT content. It can be observed that the $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ sample without NBT addition has the highest dielectric constant. However, due to the “clockwise effect”, the capacitance dropped sharply. When the amount of NBT increased from 0 to 10 mol%, the dielectric constant gradually decreased over the temperature range of -55 to 150°C. Notably, the sample with 10 mol% NBT had the lowest dielectric constant. The decreased dielectric constant is attributed to increase of NBT content. The internal stress caused by the mismatch between the core and shell of the grain might be responsible for improving the temperature dependence of the dielectric constant^[5].

CONCLUSIONS

$\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ samples with various NBT content were synthesized by two-step liquid-method. $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ was grown on the surface of NBT grains. There was secondary provskite phase detected in the samples added with NBT from the XRD patterns. But, no evidence of other phase could be seen through SEM photographs. It demonstrated that the grain had a core-shell structure. The grain size increased from 100 nm to more than 200 nm with the increase of NBT content. The sintering temperature of $\text{BaTi}_{0.9}\text{Zr}_{0.1}\text{O}_3$ ceramics could be reduced to 1100°C by doping them with NBT.

Samples had two curie points when doping with NBT. The T_c of samples at high temperature increased from 315°C to 318°C, and that at low temperature increased from 80°C to 86°C when the NBT content

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increase from 5% to 10%. The trend was caused by the diffusion between BaTi_{0.9}Zr_{0.1}O₃ and NBT, which lead to chemically inhomogeneous adulteration, diffused the curie peaks and enhanced the temperature stability.

The temperature dependence of the capacitance was -2.4%~15.1% with the NBT content of 5%, and -3.38%~21.2% with the content of 10%. So, the ceramic materials have great potential as EIA X8R-type multilayer ceramic capacitors.

ACKNOWLEDGEMENT

This work is funded by Hebei University, under contract 2008Q23, and Huazhong University of Science and Technology, under contract HF07042010185.

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