

# Dielectric properties of Mn-doped BaTiO<sub>3</sub>-based ceramics synthesized by wet chemical method

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**ABSTRACT:** A wet chemical method was used in this work to produce Ba<sub>0.985</sub>Bi<sub>0.01</sub>TiO<sub>3</sub>-BaMn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>(BBT-BMT) materials. With increasing Mn content, the ceramic capacitors display stronger temperature stability in its dielectric behavior. The dielectric properties of the samples were measured by a LCR meter. The microstructure of the ceramics was measured by a XRD. The temperature coefficient of capacitance of BBT-BMT varies from -10% to 10% while the Mn content is 0.3 at the whole range of measured temperature. Obviously, the temperature coefficient of capacitance is improved with the increase of the Mn content of compositions in the ceramics.

## INTRODUCTION

Barium titanate, BaTiO<sub>3</sub> (BT), has been the subject of intense research for several decades because it is a model system for understanding ferroelectric materials and is used in many other applications as well.[1] Ceramics, especially ferroelectrics, such as strontium titanate (SrTiO<sub>3</sub>), barium titanate (BaTiO<sub>3</sub>), and BaTiO<sub>3</sub>-based ones, have very high dielectric constants and are therefore widely used to make discrete surface mounted capacitors.[2] Those ceramics consisting of a ferroelectrics and another ferroelectrics, have attracted plenty of interest in experiments and theories. [3] Fabrication of composites that comprise ferroelectric polymers and highly polarizable fillers such as barium titanate (BaTiO<sub>3</sub>) attracted lots of attention as potential electric energy storage materials.[4] However, most work about energy storage materials is mainly focused on the fabrication of homogeneous ceramics-polymer nanocomposites and little attention has been paid to the effects of the incorporation of ceramic doped with some elements on dielectric responses and energy storage properties.[5] For both fundamental and commercial importance, tremendous efforts have been pursued to modify the dielectric and ferroelectric properties of BaTiO<sub>3</sub>-based materials by substitution. B-site substitution often comes from metal ions (Sn<sup>4+</sup>) and (Zr<sup>4+</sup> etc.).[6] The effects of Mn-substitution in BaTiO<sub>3</sub> are quite unique, and the increasing interests have been received recently.[7] However, doped MnO<sub>2</sub> can exhibit competitive ferroelectric with the benefit of being lead free. In order to ensure a better microstructural control, the classical attempts of simple composites were replaced wet-chemistry methods for in-situ preparation of the composites powders.[8] The microstructure was called the grain core and the grain shell.[9] The core-shell structure obtains good temperature stability and high dielectric constant.

In the present study, we report Ba<sub>0.985</sub>Bi<sub>0.01</sub>TiO<sub>3</sub>-BaMn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> ceramics with high temperature stability. The shell doped with different Mn content by wet chemical method. By adjusting the reaction parameter, nanocrystals with crystallite size of about 32.91 nm were obtained. The temperature coefficient of capacitance of BBT-BMT varies from -10% to 10% while the Mn content is 0.3 at the whole range of measured temperature. Obviously, the temperature coefficient of capacitance is improved with the increase of the Mn content of compositions in the ceramics.

## EXPERIMENTAL

$\text{Ba}_{0.985}\text{Bi}_{0.01}\text{TiO}_3$  powder (abbreviated BBT) were prepared using a liquid-state reaction method with pure  $\text{TiCl}_4$ ,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (AR 99.0% China),  $\text{Bi}_2\text{O}_3$  as starting materials. First,  $\text{TiCl}_4$  was hydrolyzed in stoichiometric  $\text{Bi}_2\text{O}_3$  hydrochloric acid solution to form transparent solution. Then  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was dissolved in boiling water and mixed with the above solution in a flask to form a homogeneous solution. Secondly, the mixture was heated to 95–100°C in three necked flask for 4h by heating jacket with continuous stirring. The powders were obtained after washing and drying at room temperature.

$\text{Ba}_{0.985}\text{Bi}_{0.01}\text{TiO}_3\text{-BaMn}_x\text{Ti}_{1-x}\text{O}_3$  ( $x=0, 0.01, 0.05, 0.1$ ) (BBT-BMT) powder were prepared using wet chemical method.  $\text{MnO}_2$ ,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (AR 99.0% China), pure  $\text{TiCl}_4$  as the original material. First,  $\text{TiCl}_4$  was hydrolyzed in deionized water to form transparent solution. Then  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $\text{MnO}_2$  was put in mortar with the previous paste mixed to form a homogeneous solution by pestle grinding. Finally, the BMT was coated on BBT surface to form a homogeneous solution. BBT-BMT powders were obtained after drying at room temperature. The stoichiometric information of the starting materials is shown in Table 1.

Table 1. Stoichiometric information of the starting materials for BBT-BMT

$\text{MnO}_2$	0	0.05	0.1	0.3
x				
$\text{TiCl}_4$	1	0.95	0.9	0.7
1-x				
abbreviated	BBT-BT	BBT-BMT1	BBT-BMT2	BBT-BMT3

The powders were pressed into 14 mm diameter discs with uniaxial force of approximately 10 MPa, and the final sintering conditions were 1200°C for 7.3h. Finally, the sintered discs were polished and both sides of each disc were applied silver paste to permit dielectric measurements.

The structure of the BBT-BMT powders and ceramics were determined by means of X-ray diffraction (XRD; Y-2000). The dielectric properties of ceramics were measured by a LCR meter (JS2811B) at 1 KHz. Temperature was controlled between -55 and 180 °C by high and low gimbals (GDW-150E, Changzhou Putian Instrument Manufacturing Co., Ltd.). The dielectric strength of ceramics was measured by a withstanding voltage tester (HYG-10KvA/100Kv).

## RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for  $\text{Ba}_{0.985}\text{Bi}_{0.01}\text{TiO}_3\text{-BaMn}_x\text{Ti}_{1-x}\text{O}_3$  powders ( $x=0, 0.01, 0.05, 0.1$ ). It reveals that the composite was perovskite structure. The XRD image observes with have visible second phase. The secondary phase was  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , and the relevant content will be mentioned in another papers.

Figure 2 shows SEM images of the microstructures of the Mn-doped BT ceramics with different Mn contents. The microstructure became density with increasing Mn content. It was seen that when the Mn content was gradually increasing, the density was better and better. The secondary phase with no visible were observed.

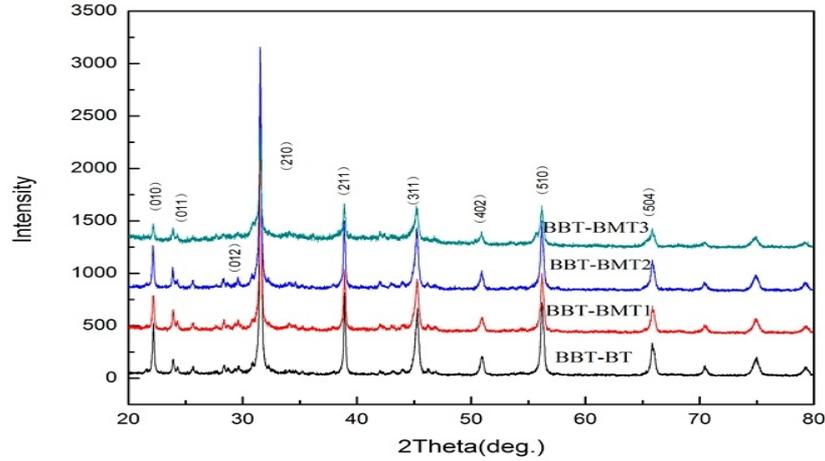


Figure 1. Room-temperature XRD powder diffraction data for BBT-BMT powders ( $x = 0, 0.01, 0.05, 0.1$ ) from bottom to top, respectively

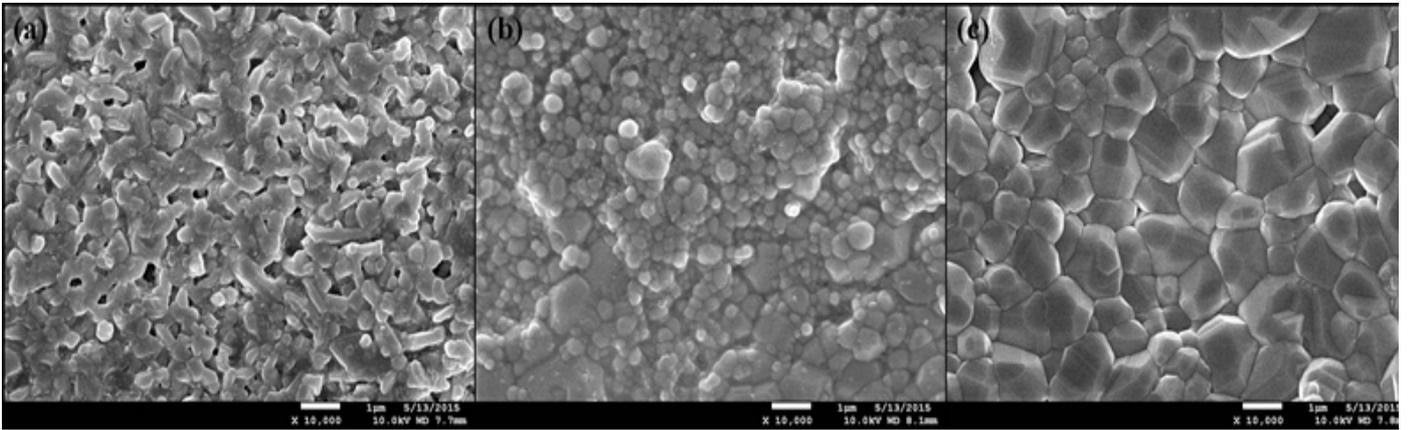


Figure 2. SEM photos of (a) BBT-BMT1, (b) BBT-BMT2, (c) BBT-BMT3

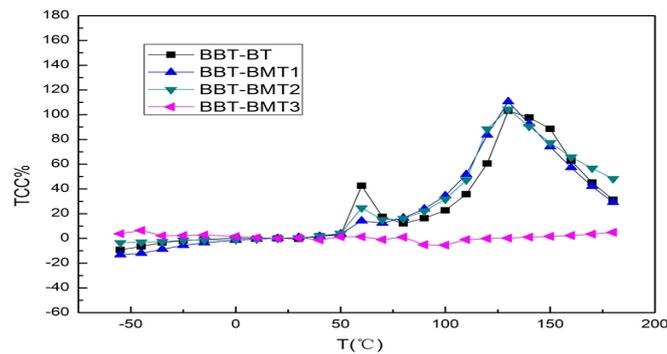


Figure 3 Temperature coefficient of capacitance of the ceramics (10 kHz) of  $\text{BaTiO}_3$ -based doped Mn,  $x=0, x=0.01, x=0.05, x=0.1$

The temperature stability of BBT-BMT ceramics as a function of temperature was shown in Figure 3. The temperature coefficient of capacitance of BBT-BMT was measured at 10 kHz with a LCR meter. The ceramics with  $x = 0$  had a poor temperature coefficient of capacitance relative to the ceramics with  $x = 0.3$ . The temperature coefficient of capacitance of BBT-BMT varies from -10% to 10% while the Mn content is 0.3 at the whole range of measured temperature. Obviously,

the temperature coefficient of capacitance is improved with the increase of the Mn content of compositions in the ceramics.

## Conclusions

Mn-doped BaTiO<sub>3</sub> (BT) powders were prepared by the wet chemical method. BBT-BMT ceramics were prepared at low temperature of 1200°C. The values of the dielectric properties decreased with increasing Mn content. Thus, as the Mn content increases, the dielectric properties will gradually decline. However, an appropriate amount of Mn doping can reduce the sintering temperature.

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