

Effects of Mg-doping on the microstructure and properties of BaTiO₃ ceramics prepared by hydrothermal method

Min Dong · Hongyan Miao · Guoqiang Tan · Yongping Pu

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Abstract Nanosized Mg-doped barium titanate powders were prepared at 240 °C by hydrothermal method using BaCl₂·2H₂O, TiCl₄ and NaOH as the main reactants and MgCl₂·6H₂O as additive. The effects of Mg-doping on microstructure and properties of BaTiO₃ ceramics were investigated by X-ray diffractometer (XRD), atomic emission spectrum (AES) and scanning electron microscopy (SEM) characterizations. As indicated by results, B site (Ti) is substituted by Mg. Mg-doping is helpful to get the microstructure with small grains and high density. Mg has evident function on shifting Curie peak. The value of ΔT_c is -40 °C in the doping range of 0 to 0.15 wt%. When Mg/Ti atomic ratio is 0.06 in starting materials, the density reaches the maximum, relative dielectric constant reaches 4,100 and breakdown electric field rises up to 3.0 kV/mm.

Keywords Barium titanate · Hydrothermal · Doping Mg

1 Introduction

Barium titanate (BaTiO₃) is a traditional perovskite-type ferroelectric. Due to its high dielectric constant, low leakage current and high breakdown electric field, BaTiO₃ is receiving extensive investigations for its potential

applications in microwave devices, dynamic random access memories (DRAM) and multi-layer capacitors. In recent years, the base metal like nickel has been commonly used as inner electrodes of multi-layer capacitors to reduce the cost. Both the BaTiO₃ dielectric layers and inner nickel electrodes must be annealed in the reducing atmosphere to avoid the oxidation of the nickel electrodes [1, 2]. However, BaTiO₃ will become semiconductive due to the oxygen vacancy when sintered in reducing or low oxygen partial pressure atmosphere [3]. The defect can affect the dielectric properties of the BaTiO₃-based devices significantly [4]. Therefore, in order to decrease the electric conductivity caused by the defect, some bivalent or trivalent elements were used to substitute Ti for charge compensation [5]. Mg²⁺ is a kind of stable bivalence acceptor ion, whose ionic radius (0.065 nm) is similar to that of Ti⁴⁺ (0.068 nm), and it can replace Ti in B site of ABO₃ structure [6, 7]. At present, BaTiO₃ powders have been synthesized by solid-state reaction, sol-gel method, the alkoxide method and the hydrothermal method. Among them, hydrothermal method is a commercial way to prepare nanosized BaTiO₃ powders [8, 9]. In this paper, nanosized Mg-doped BaTiO₃ powders were synthesized by hydrothermal method and the dielectric properties of the Mg-doped BaTiO₃ ceramics were studied.

2 Experimental procedure

2.1 Samples preparation

BaCl₂·2H₂O and TiCl₄ were used as barium and titanium precursors, respectively. NaOH was used as mineralizer. All the chemical reagents used were of analytical grade. Initially, TiCl₄ was slowly added to ice-cold water, with a

M. Dong · H. Miao (✉) · G. Tan
School of Materials Science and Engineering,
Shaanxi University of Science and Technology,
Xianyang 712081, People's Republic of China
e-mail: mhy@sust.edu.cn

Y. Pu
State Key Laboratory of Electrical Insulation for Power
Equipment, Xi'an Jiaotong University,
Xi'an 710049, People's Republic of China

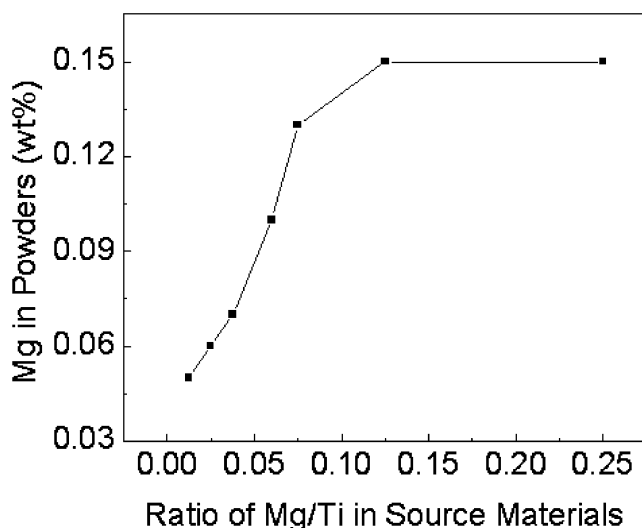


Fig. 1 The dependence of Mg content on Mg/Ti atomic ratio in starting materials

target concentration of 0.6 M. Subsequently, TiCl_4 solution of the stated concentration was slowly added into the BaCl_2 solution with stirring. In all runs, a stoichiometric Ba/Ti ratio of 2.0 was employed. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added as the source of magnesium. The excess of NaOH concentration was fixed at 2 M. The hydrothermal reaction was carried out at 220–260 °C for 10–16 h in a 50 ml Teflon-lined autoclave with a filling capacity of 60%. After the reaction, the particles were washed, filtered and dried overnight at 90 °C. And then, the powders were dry-pressed to bodies of $\varnothing 14 \times 2$ mm and sintered at 1275 °C for 2 h. At last, silver electrodes were prepared on the BaTiO_3 ceramics samples for dielectric properties measurements.

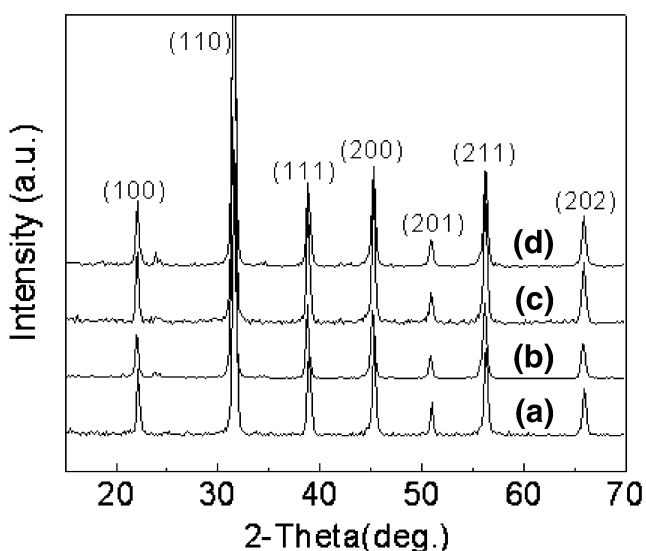


Fig. 2 XRD patterns of BaTiO_3 powders with various Mg/Ti atomic ratios (240 °C) r (Mg/Ti): (a) 0.06, (b) 0.08, (c) 0.10, (d) 0.15

Table 1 Each percentage by weight of Ba, Ti and Mg.

No.	r (Mg/Ti)	Ba (wt%)	Ti (wt%)	Mg (wt%)
1	0	53.3	20.9	0
2	0.02	52.4	22.8	0.0545
3	0.06	52.2	18.7	0.1144
4	0.08	53.5	18.2	0.1304
5	0.10	52.8	17.9	0.1412

2.2 Characterizations

The crystal phase and lattice parameters of powders were determined by a Rigaku D/max-2200PC rotating X-ray diffractometer (XRD). The analysis was performed at 40 kV and 60 mA with Ni-filtered $\text{Cu-K}\alpha$ radiation, 2θ in the range 15–70° with a step of 0.02°. The elements compositions were analyzed by an Integra XL atomic emission spectrum (AES). The morphologies of BaTiO_3 powders as well as ceramics were observed by a Philips XL20 scanning electron microscopy (SEM). The relative dielectric constant was measured by a HP 4284A LCR meter with a frequency of 1 kHz. The breakdown electric field was measured by an alternating breakdown device.

3 Results and discussion

Figure 1 shows a relationship between Mg content included in the particles and Mg/Ti atomic ratio in source materials. In this study, we defined Mg content as a percentage by weight. Mg content increased with increasing Mg/Ti atomic ratio below Mg/Ti atomic ratio of 0.13, and became almost constant around 0.15 wt% above Mg/Ti atomic ratio of 0.13, which suggested that the maximum of Mg content in

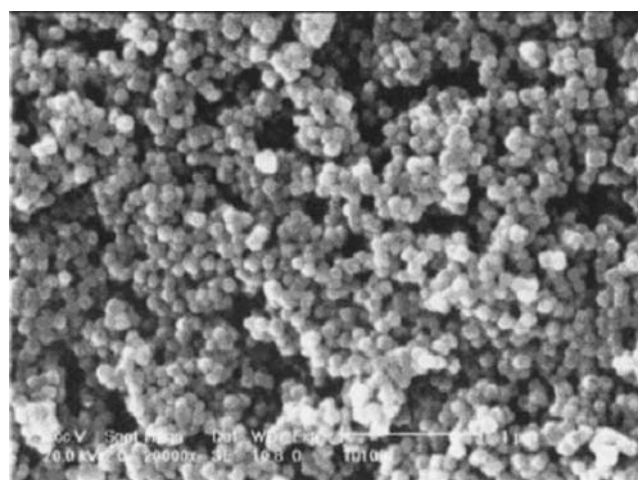
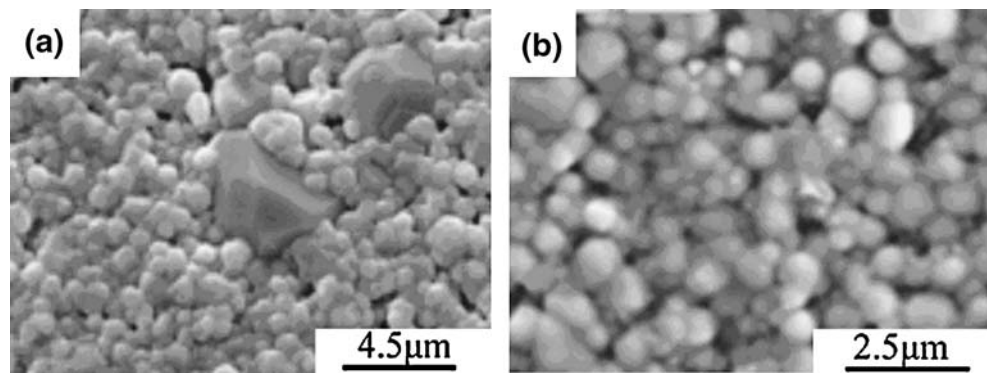


Fig. 3 SEM micrograph of the BaTiO_3 powders with a Mg/Ti atomic ratio of 0.06

Fig. 4 SEM micrographs of (a) BaTiO_3 and (b) MgO-BaTiO_3 ceramics sintered at 1275°C for 2 h



solid solution of MgO-BaTiO_3 system under the condition used in the study was about 0.15 wt%. Thus, we could prepare the samples with various Mg contents from 0 to 0.15 wt%.

XRD measurement was used to confirm whether Mg entered really into the BaTiO_3 lattice or existed as the secondary phase besides BaTiO_3 powders. From Fig. 2, the XRD patterns of the BaTiO_3 powders with various ratios, all as-prepared hydrothermal powders could be indexed by perovskite BaTiO_3 phase but a slight extra diffraction peak belonging to BaCO_3 was observed, which indicated that addition of Mg did not produce new phase such as MgO , MgCl_2 or MgTiO_3 in doping concentration range of experiment. Table 1 shows each percentage by weight of Ba, Ti and Mg measured using AES analysis. In Table 1, the percentage of Ba fluctuated little regardless of Mg contents. On the other hand, the percentage of Ti decreased with increasing weight percentage of Mg. The above results revealed a fact that Mg did not exist as the secondary phase besides BaTiO_3 , but existed substitutionally in Ti site of a BaTiO_3 lattice.

Figure 3 shows the SEM micrograph of the hydrothermal BaTiO_3 powders with a Mg/Ti atomic ratio of 0.06 in starting materials. It was indicated that the grains were well crystallized and dispersed. The grains were spherical and the grain size ranged from 60 to 125 nm.

Fine grains and high density of ceramics body are considerably important to high voltage ceramic media. Abnormal growth of BaTiO_3 crystallites may reduce dielectric constant of ceramics. Increasing of pores and impurity phases may also lead to a greater dielectric loss. Doping a certain amount of proper elements, especially acceptors, can improve sintering and advance density effectively to obtain homogenous microstructure with small grain, which may affect electric properties of BaTiO_3 ceramics strongly [7]. Figure 4 shows the SEM micrographs of the BaTiO_3 and MgO-BaTiO_3 ceramics. BaTiO_3 ceramics was not uniform and some large grains were observed. While for the MgO-BaTiO_3 ceramics, when Mg/Ti atomic ratio was 0.06 in starting materials, which was the optimized dopant concentration, the grains were well

distributed in size of 500 nm and no large grains were caused by abnormal growth.

Figure 5 is the curve of dielectric constant versus temperature of MgO-BaTiO_3 ceramics sintered at 1275°C . In the curve, the shift of the Curie peak to lower temperature was observed. The Curie temperature T_c of the MgO-BaTiO_3 ceramics, the phase transition temperature from paraelectric to ferroelectric, was about 80°C but that of pure BaTiO_3 ceramics was 120°C . The value of ΔT_c was -40°C in the doping range of 0 to 0.15 wt%, and the substitution content of Mg in BaTiO_3 solid solution reached the saturated state when referring to a higher content. When Mg/Ti atomic ratio was 0.06 in starting materials, MgO-BaTiO_3 ceramics showed a higher dielectric constant up to 4,100 at room temperature. Furthermore, for the MgO-BaTiO_3 ceramics specimen with Mg/Ti=0.06, the dielectric constant was the most stable and its variation range was $\pm 10\%$ at a temperature range of -15 to 100°C . It was also indicated that the excess Mg dopant could decrease the peak value of dielectric constant of the MgO-BaTiO_3 ceramics.

It is known that the breakdown electric field of the BaTiO_3 ceramics increased with the decrease of grain size.

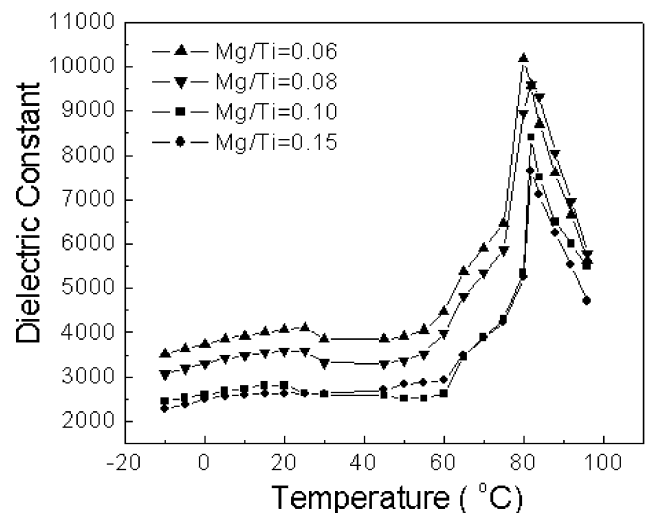


Fig. 5 The curve of dielectric constant vs temperature of MgO-BaTiO_3 ceramics sintered at 1275°C

Our test result showed that breakdown electric field of the MgO–BaTiO₃ ceramics increased rapidly with increasing of sintering temperature. Without any sintering aids, the breakdown electric field of MgO–BaTiO₃ ceramics was up to 3.0 kV/mm. Compared the value of 2.6 kV/mm for pure BaTiO₃ ceramics, the significant rise of breakdown electric field was believed to be resulted from the fine grain size of the MgO–BaTiO₃ ceramics.

4 Conclusions

Mg-doped barium titanate nanosized powders were prepared by hydrothermal method at 240 °C with BaCl₂·2H₂O, TiCl₄ and NaOH as the main reactants and MgCl₂·6H₂O as dopant. In the Mg doping range of experiments, no secondary phase or impurities were detected in the as-prepared BaTiO₃ powders. Mg, as a kind of acceptor, entered into the BaTiO₃ lattice and existed substitutionally in Ti site, which made the ceramics exhibit a microstructure with small grains and high density. With the increase of Mg dopant from 0 to 0.15 wt%, the Curie point shifted to lower temperature of about 80 °C. The optimized ratio of Mg/Ti was 0.06, and the MgO–BaTiO₃ ceramics showed high

dielectric constant up to 4,100 and high breakdown electric field of 3.0 kV/mm. However, the dielectric constant of the MgO–BaTiO₃ ceramics decreased when excess Mg dopant was used.

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