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# Doping effects of Dy and Mg on $BaTiO_3$ ceramics prepared by hydrothermal method

**Hongyan Miao · Min Dong · Guoqiang Tan · Yongping Pu**



**Abstract** Fine Dy and Mg-doped barium titanate powders were prepared by hydrothermal method at 240°C with $BaCl_2{\cdot}2H_2O$, $TiCl_4$ and NaOH as the main reactants, $Dy_2O_3$ and $MgCl_2{\cdot}6H_2O$ as additives respectively. The substitution style, microstructure and electrical properties of the two kinds of samples were comparatively studied by X-ray diffractometer (XRD), atomic emission spectrum (AES) and scanning electron microscopy (SEM) characterizations. It is confirmed that Dy or Mg enters into the $BaTiO_3$ lattice. Ba site is replaced if a little $Dy_2O_3$ is doped but some more Dy will take up the positions of Ti. Mg always substitutes for Ti site. Dy and Mg are both useful to obtain the microstructure with small grains and high density, and the former results in a better microstructure. Dy has no influence on shifting and depressing Curie peak. When $Dy_2O_3$ content is 0.6 wt%, the dielectric constant rises up to 4250. However, Mg has evident effect on shifting Curie peak. The value of $\Delta T_c$ is −40°C in the doping range of 0 to 0.15 wt%. When Mg/Ti atomic ratio is 0.06 in the precursors, the dielectric constant rises up to 4100.

**Keywords** Barium titanate · Hydrothermal · Dy · Mg

## 1 Introduction

Barium titanate ($BaTiO_3$) is the best-known perovskite material and has been broadly used as the raw material for ceramic condensers, memory, and multi-layer ceramic capacitors. At present, hydrothermal synthesis is considered as one of the best methods used to prepare monodisperse nanometer $BaTiO_3$ powders, which presents the following major advantages: narrow particle size distribution, low coacervation, high purity and fine crystallization of powders, little pollution during the preparation process, short preparation time and low cost [1, 2].

The soft mode of $BaTiO_3$ is Slater mode (= stretching vibration between Ti and $O_6$ octahedra), and the defects on Ba and Ti site can affect the soft mode significantly [3]. For this purpose, the addition of Dy, which is a kind of rare earth elements, and Mg, whose ionic radius (0.065 nm) is similar to that of $Ti^{4+}$ [4, 5], into hydrothermal $BaTiO_3$ particles were chosen to modify the ceramic properties. Moreover, we discussed doping effects of Dy and Mg on $BaTiO_3$ ceramics through XRD, SEM and AES analysis.

## 2 Experimental procedure

### 2.1 Samples preparation

$BaCl_2{\cdot}2H_2O$ and $TiCl_4$ were used as precursors, and NaOH was used as mineralizer. All the chemical reagents used were of analytical grade. Initially, $TiCl_4$ was slowly added to icy water to prepare 0.6 M $TiCl_4$ aqueous solution. Subsequently, $TiCl_4$ solution was slowly added into $BaCl_2$ aqueous solution with continuously stirring. The atomic ratio of Ba/Ti was kept at 2.0. Then, $MgCl_2{\cdot}6H_2O$ and $Dy_2O_3$ were added as the sources of magnesium and dysprosium, respectively. The excess NaOH concentration was fixed at 2 M. At last, the mixed precursor solution was sealed in a 50 ml Teflon-lined autoclave with a filling capacity of 60% and soaked at 220–260°C for 10–16 h. After the reaction, the autoclave was cooled naturally to room temperature. The

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

powders were washed by distilled water until no $Cl^-$ was detected by $AgNO_3$. The powders were dried at 90°C and then ball-milled for 4 h before use. Samples in Φ14 mm × 2 mm were prepared by dry press and then were sintered at 1275°C for 2 h. At last, silver electrodes were prepared on the $BaTiO_3$ ceramics samples for dielectric properties measurements.

### 2.2 Characterizations

The phase and lattice parameters of the powders were determined by a Rigaku D/max-rA roating X-ray diffractometer (XRD). The analysis was performed at 40 kV and 60 mA with Ni-filtered Cu-K$\alpha$ radiation. The compositions of the $BaTiO_3$ powders were analyzed by a JY-38plus atomic emission spectrum (AES). The morphologies of $BaTiO_3$ powders as well as $BaTiO_3$ ceramics were observed by a PHILIPS XL20 scanning electron microscopy (SEM). Dielectric constant was measured by a Taiwan HE2612 capacitor meter with a test frequency of 1 kHz. The breakdown electric field was measured by an alternating breakdown device.

## 3 Results and discussion

According to the theory of crystal chemistry, in an ideal perovskite, the ionic radius, $r_i$ ($i$ = A, B, O), satisfies the equation: $(r_A + r_O) = \sqrt{2}(r_B + r_O)$ [6]. The Goldschmidt tolerance factor for perovskites is, hence, defined by

$$t = (r_A + r_O)/\sqrt{2}\,(r_B + r_O) \tag{1}$$

$r_A, r_B$ and $r_O$ respectively represent the radii of A, B position and oxygen ion in the $ABO_3$ structure. The tolerance factor of $Dy^{3+}$ is 0.87 in A site and 0.89 in B site. Due to their similarity, Dy can replace A and B positions in a certain proportion.

Figure 1 shows the effect of $Dy_2O_3$ dopant on the lattice parameters of the $Dy_2O_3$-$BaTiO_3$ powders. The lattice parameters were calculated from miller indexes obtained by XRD patterns data. When small amount of $Dy_2O_3$ was doped, the lattice cell parameters decreased sharply, which indicated that Ba was replaced by Dy because ionic radius of $Dy^{3+}$ is smaller than $Ba^{2+}$(= 1.61Å). However, with increasing amount of the $Dy_2O_3$ dopant, the values of $a$ and $c$ increased gradually and then leveled off. It indicated that some Dy ions also occupied the positions of Ti because ionic radius of $Dy^{3+}$ is larger than $Ti^{4+}$(= 0.68Å). When the amount of $Dy_2O_3$ dopant increased to 0.6 wt%, the lattice parameters of the $Dy_2O_3$-$BaTiO_3$ reached the maximum. The above cases conformed the following substituting mechanism (2) and (3) respectively:

$$x\mathrm{Dy}^{3+} + \mathrm{BaTiO_3} \rightarrow \left(\mathrm{Ba}^{2+}_{1-x}\mathrm{Dy}^{3+}_{x}\right)\left[\mathrm{Ti}^{4+}_{1-x}(\mathrm{Ti}^{4+} \bullet \mathrm{e})_x\right]\mathrm{O_3} + x\mathrm{Ba}^{2+} \tag{2}$$

$$x\mathrm{Dy}^{3+} + \mathrm{BaTiO_3} \rightarrow \mathrm{Ba}^{2+}_{1-x/2}\mathrm{Dy}^{3+}_{x}\left(\mathrm{Ti}^{4+}_{1-x/2}\right)\mathrm{O_3} + x/2\mathrm{Ba}^{2+} + x/2\mathrm{Ti}^{4+} \tag{3}$$

The judging method of lattice parameters is unreliable to Mg dopant because its radius (0.065 nm) is similar to that of $Ti^{4+}$ (0.068 nm). In order to confirm whether Mg entered really into the $BaTiO_3$ lattice or existed as the secondary phase besides $BaTiO_3$, XRD measurement of the powders was performed. Figure 2 is XRD patterns of MgO-$BaTiO_3$ powders with various Mg/Ti atomic ratios. From XRD results, most as-prepared hydrothermal particles were assigned to $BaTiO_3$phase and there was only a slight extra diffraction peak belonging to $BaCO_3$, which indicated that the Mg dopant did not form other new phases such as MgO, $MgCl_2$ or $MgTiO_3$ in doping concentration range of our experiments. Table 1 shows each weight percentage of Ba, Ti and Mg measured using AES analysis. In Table 1, 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 $BaTiO_3$ in the particles, but existed substitutionally in Ti site of a $BaTiO_3$ lattice.

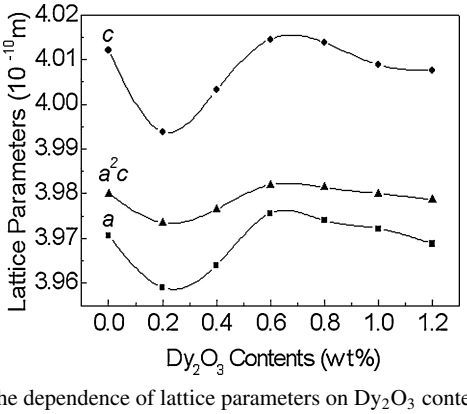


**Fig. 1** The dependence of lattice parameters on $Dy_2O_3$ contents

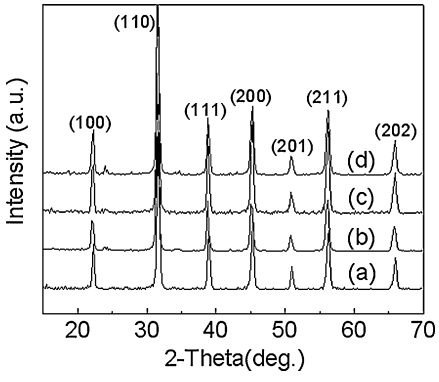


**Fig. 2** XRD patterns of MgO-$BaTiO_3$ powders with various Mg/Ti atomic ratios (240°C) Mg/Ti: (a) 0.06 (b) 0.08 (c) 0.10 (d) 0.15

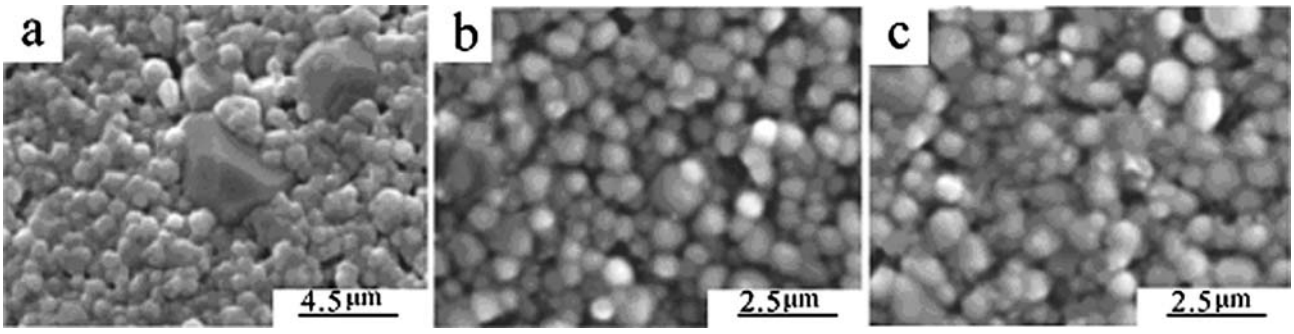


**Fig. 3** SEM micrographs of (a) $BaTiO_3$, (b) $Dy_2O_3$-$BaTiO_3$ and (c) MgO-$BaTiO_3$ ceramics sintered at 1275°C

Figure 3 shows the micrographs of the (a) $BaTiO_3$, (b) $Dy_2O_3$-$BaTiO_3$ and (c) MgO-$BaTiO_3$ ceramics. From Fig. 3(a), the pure $BaTiO_3$ ceramics was not uniform in grain size distribution and some large grains were observed, which can affect electric properties of $BaTiO_3$ ceramics strongly [7–9]. With doping of additives, the grains became smaller, the density became higher, and the cracks and pores accumulation gradually disappeared. Figure 3(b) and (c) are micrographs of $BaTiO_3$ ceramic surface including Dy and Mg respectively in optimized doping conditions. In Fig. 3(b), $Dy_2O_3$ content was 0.6 wt%. Grains were well distributed in size of 480 nm and had no abnormal growth. In Fig. 3(c), the best doping condition was 0.06 at Mg/Ti atomic ratio. The surface appearance of (b) was better than that of (c), in which grain size was about 500 nm. Furthermore, MgO-$BaTiO_3$ ceramics exhibited a little non-uniform size distribution with slight abnormal growth of grains. We can get a conclusion that $Dy_2O_3$, compared MgO, is a more excellent kind of growth-constraining agents, which make ceramic materials have microstructure with small grains.

Figure 4 is the curve of dielectric constant versus temperature of $Dy_2O_3$-$BaTiO_3$ ceramics sintered at 1275°C, which expresses the effects of Dy content on ceramic electric properties. From the curve, we can believe that in the doping range of Dy, doped ceramics' dielectric character was similar to the pure $BaTiO_3$ and Curie temperature changed little. It meant that Dy had no evident function on shifting and depressing Curie peak. When $Dy_2O_3$ content was 0.6 wt%, the dielectric constant rose to 4250 at room temperature.

From dielectric characteristics of $BaTiO_3$ ceramics including various Mg in Fig. 5, with increasing of the Mg/Ti atomic ratio, the shift of the peaks to lower temperature was observed. The Curie temperature $T_c$ of the MgO-$BaTiO_3$ ceramics was about 80°C but that of pure $BaTiO_3$ ceramics was 120°C. The value of $\Delta T_c$ was −40°C in the doping range of 0 to 0.15 wt%, and the substitution content of Mg

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

| No. | 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 |

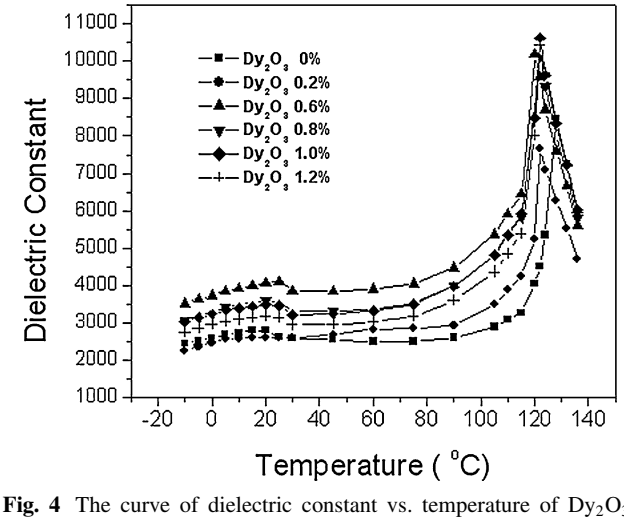


**Fig. 4** The curve of dielectric constant vs. temperature of $Dy_2O_3$-$BaTiO_3$ ceramics sintered at 1275°C

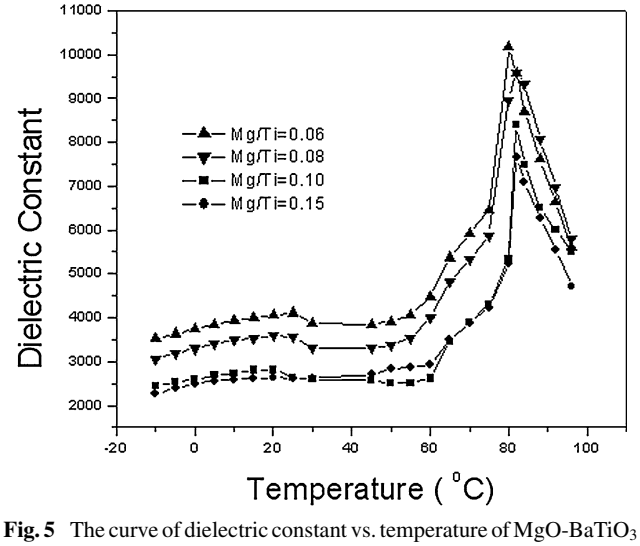


**Fig. 5** The curve of dielectric constant vs. temperature of MgO-$BaTiO_3$ ceramics sintered at 1275°C

in $BaTiO_3$ solid solution reached the saturated state when referring to a higher content. When Mg/Ti atomic ratio was 0.06, MgO-$BaTiO_3$ ceramics specimen performed a higher dielectric constant of 4100 at room temperature. It was also indicated that the excess Mg could also depress peak value of dielectric constant sometimes.

From Figs. 4 and 5, we can calculate that when $Dy_2O_3$ content was 0.6 wt% or Mg/Ti atomic ratio was 0.06, dielectric constant was the most stable and changed between –10% and 10% at a temperature range of –15 – 100°C. Besides these, our test results also show that, without any sintering aids, the breakdown electric field of $BaTiO_3$ ceramics including Mg and Dy were up to 3.2 kV/mm and 3.0 kV/mm respectively. Compared the value of 2.6 kV/mm for pure $BaTiO_3$ ceramics, the significant rise of breakdown electric field was due to the obtained small-grain microstructure by doping Dy or Mg.

## 4 Conclusions

Barium titanate powders including various Dy and Mg were prepared by hydrothermal method at 240°C with $BaCl_2 \cdot 2H_2O$, $TiCl_4$ and NaOH as the main reactants, $Dy_2O_3$ and $MgCl_2 \cdot 6H_2O$ as dopants respectively. In our experiment conditions, Dy or Mg entered into the $BaTiO_3$ lattice. Ba site was replaced if a little $Dy_2O_3$ was doped. But when the $Dy_2O_3$ content increased, some Dy ions would take up the positions of Ti. Mg substituted for Ti site all the time because of its similar ionic radius to $Ti^{4+}$. Dy and Mg were both useful to constrain the growth of the grains and obtain the microstructure with small grains and high density, and $Dy_2O_3$-$BaTiO_3$ exhibited a better microstructure. $Dy_2O_3$ had no evident influence on shifting and depressing Curie peak. When $Dy_2O_3$ content was 0.6 wt%, the dielectric constant rose up to 4250. However, Mg had evident function on shifting Curie peak, and the Curie temperature shifted to lower temperature of 80°C. When Mg/Ti atomic ratio was 0.06, the dielectric constant was up to 4100. In the above two cases, dielectric constants were both much stable and its variation range was ±10% at –15–100°C. The microstructure with small grains and high-density, obtained by doping Dy and Mg, caused breakdown electric field to rise up to 3.2 kV/mm and 3.0 kV/mm respectively without any sintering aids.

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