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Studies of resistivity and dielectric properties of magnesium doped barium titanate sintered in pure nitrogen

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Abstract This paper investigated resistivity and dielectric properties of magnesium doped $BaTiO_3$. Influence of variable doping concentration and Ba/Ti ratio on densification, microstructure, resistivity and dielectric properties was studied. Ceramics sintered in pure nitrogen had higher apparent density than that of ceramics sintered in air. Second phase occurred when Mg doping concentration was greater than 2 mol%. Ceramics sintered in pure nitrogen had higher resistivity than ceramics sintered in air when A/B ratio ≥1. When Ba/Ti ratio was equal to 1.01, resistivity of the samples sintered in pure nitrogen increased with doping concentration increasing. Dielectric constant changed little with doping concentration increasing, but leakage conductivity decreased much. Samples with Ba/Ti ratio of 1.005 had the largest dielectric constant irrespective of doping concentration.

Keywords Barium titanate · Hydrothermal · Pure nitrogen · Resistivity · Dielectric properties

1 Introduction

Recently multilayer ceramic capacitors (MLCCs) with internal electrodes made of a base metal such as Ni has been developed in an effort to reduce costs [1–5]. A nickel internal electrode is easily oxidized during firing under ambient conditions. Therefore, dielectric and internal electrode cofiring should be carried out in a reducing atmosphere. However, barium titanate ceramics tend to become semiconducting after being heated in an atmosphere of low O_2 content [1–3, 6]. Increasing in conductivity has been explained by formation of oxygen vacancies and accompanying reduction of tetravalent titanate to trivalent state, which can be compensated by incorporating a small amount of trivalent or divalent dopant on titanate sites [7, 8].

As stable divalent acceptors, magnesium ions on Ti-sites have been reported as strong acceptors under the reducing condition [8]. Kishi et al. [9] reported that magnesium ions incorporated into Ti sites, and solubility limit for $\left[\mathrm{Mg}^{2+}{}_{\mathrm{Ti}}\right]''$ is about 2.0 mol% [10].

This paper investigated solubility limit for magnesium in $BaTiO_3$ lattice when Ba/Ti ratio was equal to 1.01 and sintering atmosphere was pure nitrogen. And influence of variable doping concentration and Ba/Ti ratio on densification, microstructure, resistivity and dielectric properties for Mg doped $BaTiO_3$ was studied.

2 Experimental procedure

Formulations of the samples were prepared according to Table 1.

Sample preparation was performed by conventional powder processing method, including ball-milling, drying, uniaxially pressing, and finally sintering in pure nitrogen. The starting materials were hydrothermally synthesized $BaTiO_3$ and highly pure oxides (Reagent grade), $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, $Ba(CH_3OO)_2$. Before mixing with the dopants, hydrothermal $BaTiO_3$ was calcined at 1000°C to remove water and defects within it. The oxides dopants and the calcined hydrothermal $BaTiO_3$ were mixed by wet ball milling using deionized water and ZrO_2 balls (∅ 3 mm), then fired at 950°C for 2 h to promote diffusion

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Table 1 Compositions and densities of the samples.

Serial number	Composition	Density (g/cm^3)	
		Nitrogen	Air
BTMg1	$Ba_{1.01}(Ti_{0.99}Mg_{0.01})O_{3.01}$	5.77	5.76
BTMg2	$Ba_{1.01}(Ti_{0.98}Mg_{0.02})O_{3.01}$	5.79	5.77
BTMg3	$Ba_{1.01}(Ti_{0.96}Mg_{0.04})O_{3.01}$	5.7	5.58
BTMg4	$Ba_{1.01}(Ti_{0.92}Mg_{0.08})O_{3.01}$	5.62	5.58
BTMg5	$Ba_{1.005}(Ti_{0.99}Mg_{0.01})O_{2.995}$	5.69	5.59
BTMg6	$Ba_{1.01}(Ti_{0.99}Mg_{0.01})O_{3}$	5.61	5.36
BTMg7	$Ba_{1.005}(Ti_{0.98}Mg_{0.02})O_{2.985}$	5.72	5.62
BTMg8	$Ba_{1.01}(Ti_{0.98}Mg_{0.02})O_{2.99}$	5.48	5.43

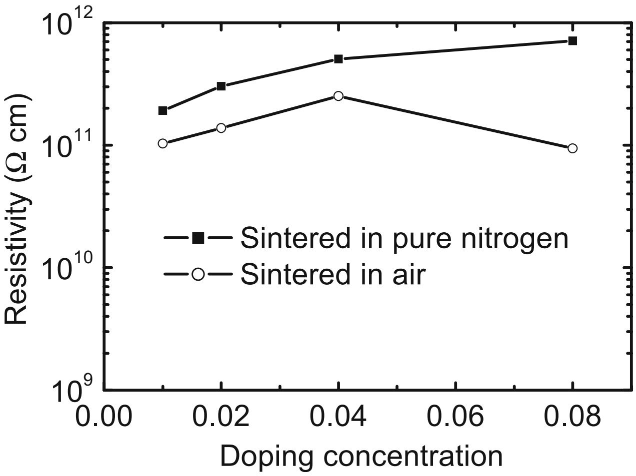

Fig. 2 Influence of doping concentration and sintering atmosphere on resistivity of Mg doped $BaTiO_3$ [$Ba_{1.01}(Ti_{1-x}Mg_x)O_{3.01}$ x=0.01, 0.02, 0.04, 0.08]

of dopants. The calcined powders were then uniaxially pressed into disks with 10 mm in diameter and 1 mm in thickness. Then the disks were sintered in pure nitrogen at various temperatures after the binder was burned out in air. After sintering, silver electrode was coated on both sides of specimens for electrical measurements. Then, the samples with silver electrode were calcined at 520°C in air. Microstructures of ceramics were studied on the as-fired surfaces of the sintered ceramics using SEM (JEOL JSM-5510LV) with an accelerating voltage of 10 kV.

Dielectric properties of sintered disk were measured from −60 to 160°C with an impedance analyzer LCR (HP 4284A) at 1 kHz with an oscillation level of 1 V rms. The heating rate was 2°C/min and the accuracy was 0.1°C.

After sintering, apparent density of the samples were determined by the Archimedes method. Insulation resistivities were investigated by means of a high resistance meter (Keithley 6517A) using an alternating polarity resistance test method. The alternating polarity resistance was designed to improve high resistance measurements and it was possible to eliminate the effects of background currents. The test voltage was 100 V.

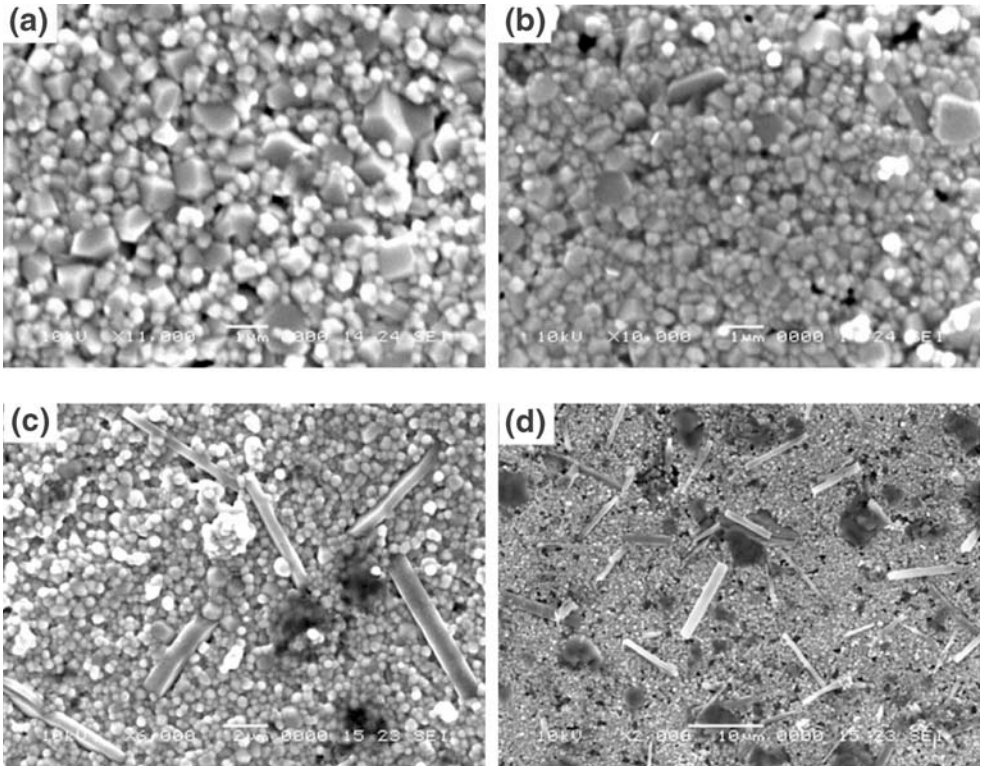

Fig. 1 SEM morphology of four as-fired ceramics sintered in 1250°C with a soak time of 3 h: (**a**) $Ba_{1.01}(Ti_{0.99}Mg_{0.01})O_{3.01}$ (**b**) $Ba_{1.01}(Ti_{0.98}Mg_{0.02})O_{3.01}$ (**c**) $Ba_{1.01}(Ti_{0.96}Mg_{0.04})O_{3.01}$ (**d**) $Ba_{1.01}(Ti_{0.92}Mg_{0.08})O_{3.01}$

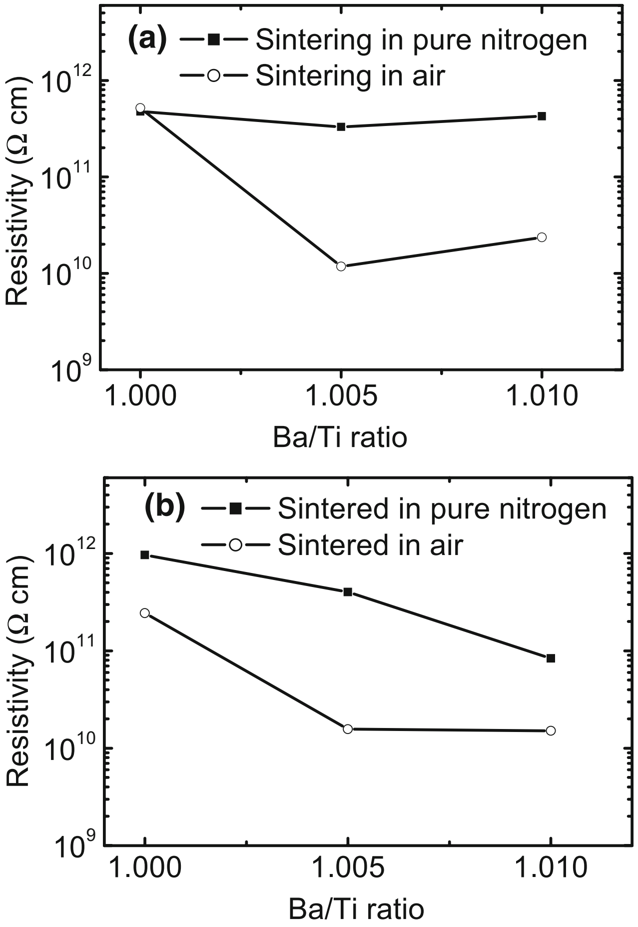

Fig. 3 Influence of Ba/Ti ratio and sintering atmosphere on resistivity of Mg doped $BaTiO_3$: (**a**) Mg (1 mol%) on Ti-site, (**b**) Mg (2 mol%) on Ti-site

3 Results and discussion

3.1 Sintering density

When barium titanate ceramics sintered in a low O_2 content atmosphere, a large number of oxygen vacancies would be produced. These oxygen vacancies have important influences on the densification process. Table 1 shows the influence of sintering atmosphere on the densification of Mg doped $BaTiO_3$. As seen from Table 1, we obtained the result that ceramics sintered in pure nitrogen had higher apparent density than ceramics sintered in air. When ceramics sintered in pure nitrogen, a larger number of oxygen vacancies would be produced compared with the ceramics sintered in air. These oxygen vacancies are favorable to atomic diffusion of solid reaction. At the same time, they promote the densification process. Therefore, when sintering temperature and the soak time were fixed, samples sintered in pure nitrogen had higher apparent density than samples sintered in air.

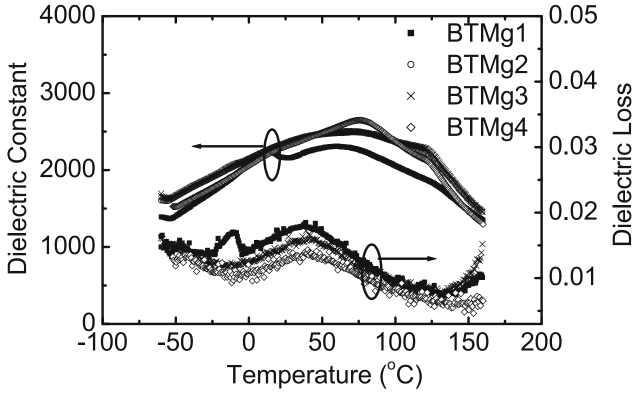

Fig. 4 Influence of doping concentration on the dielectric properties for Mg doped $BaTiO_3$ $[Ba_{1.01}(Ti_{1-x}Mg_x)O_{3.01}$ x=0.01, 0.02, 0.04, 0.08]

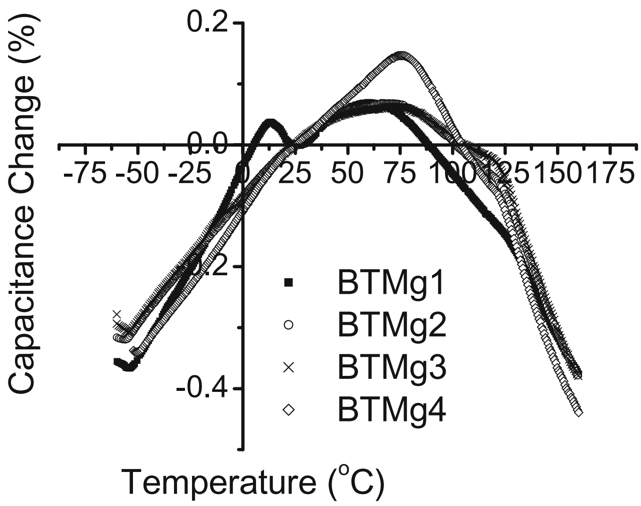

Fig. 5 Temperature coefficient of capacitance for Mg doped $BaTiO_3$ sintered in pure nitrogen $[Ba_{1.01}(Ti_{1-x}Mg_x)O_{3.01}$ x=0.01, 0.02, 0.04, 0.08]

3.2 Microstructure development

According to literature, solubility for magnesium ions on Ti-sites was not high. Kishi et al. [9] reported that solubility limit for $\left[Mg^{2+}{}_{Ti}\right]''$ was about 2.0 mol% [10]. Figure 1

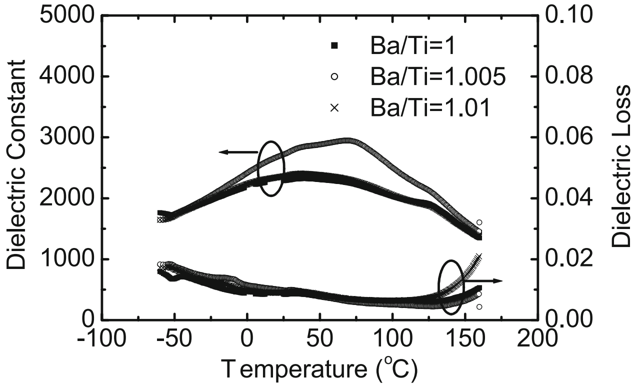

Fig. 6 Influence of Ba/Ti ratio on the dielectric properties for Mg (1 mol %) in Ti site

shows SEM morphology of four as-fired ceramics [$Ba_{1.01}(Ti_{1-x}Mg_x)O_{3.01}$ x=0.01, 0.02, 0.04, 0.08, specified by BTMg1–4] sintered in 1250°C with a soak time of 3 h. As seen from Fig. 1, second phase occurred in BTMg3 and BTMg4. With magnesium ions content increasing, the magnitude of the second phase increased.

3.3 Resistivity properties of as-fired ceramics

Sintering atmosphere has an important influence on resistivity of magnesium doped barium titanate. Figure 2 illustrates the influence of doping concentration and sintering atmosphere on resistivity of magnesium doped barium titanate. Figure 3 shows the influence of Ba/Ti ratio and sintering atmosphere on resistivity of magnesium doped $BaTiO_3$. Generally, for samples A/B with ratio ≥1, ceramics sintered in pure nitrogen had higher resistivity than that of ceramics sintered in air. The difference was up to 1–2 orders of magnitude. As seen from Fig. 2, when Ba/Ti ratio was equal to 1.01, resistivity of samples sintered in pure nitrogen increases with doping concentration increasing. However, resistivity of samples sintered in air reached maximum with doping concentration of 4 mol%. According to Fig. 3, when a sintering atmosphere was pure nitrogen and doping concentration was 1 mol%, resistivity almost did not change with Ba/Ti ratio. And when a sintering atmosphere was pure nitrogen and doping concentration was 2 mol%, resistivity decreased with increasing Ba/Ti ratio. When sintering atmosphere was air, Ba/Ti ratio had an important effect on resistivity when Ba/Ti ratio value increased from 1.0 to 1.005, resistivity decreased sharply, and when Ba/Ti ratio value varied between 1.005 and 1.01, resistivity changed little.

3.4 Dielectric properties of as-fired ceramics

Figure 4 shows the influence of doping concentration on the dielectric properties for Mg doped $BaTiO_3$. The temperature coefficient of capacitance (TCC) for Mg doped $BaTiO_3$ sintered in pure nitrogen is illustrated in Fig. 5. As seen from Fig. 4, dielectric constant did not change very much with doping concentration increasing, but leakage conductivity decreased. This agrees well with resistivity measurement. We can see from Fig. 5, the temperature coefficient of capacitance (TCC) for Mg doped $BaTiO_3$ sintered in pure nitrogen satisfy the Y5V specification of EIA (TCC within +22 to 82% from −30 to +85°C). Figure 6 shows the influence of Ba/Ti ratio on the dielectric properties for samples with Mg (1 mol%) on Ti-sites. Samples with Ba/Ti ratio of 1.005 had the largest dielectric constant irrespective of doping concentration. The leakage conduction did not change very much, which agrees with resistivity measurement.

4 Conclusions

This paper investigated resistivity and dielectric properties of magnesium doped $BaTiO_3$. The influence of variable doping concentration and Ba/Ti ratio on densification, microstructure, resistivity and dielectric properties was studied.

1. Ceramics sintered in pure nitrogen had higher apparent density than that of ceramics sintered in air.
2. A second phase occurred when Mg doping concentration >2 mol%.
3. Ceramics sintered in pure nitrogen had higher resistivity than that of ceramics sintered in air for samples with A/B ratio ≥1. When Ba/Ti ratio was equal to 1.01, resistivity of samples sintered in pure nitrogen increased with Mg doping concentration increasing.
4. Dielectric constant did not change very much with doping concentration increasing, but leakage conductivity decreased much. Samples with Ba/Ti ratio of 1.005 had the highest dielectric constant irrespective of doping concentration.

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