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Dielectric properties of $BaTiO_3$-based ceramics sintered in reducing atmospheres prepared from nano-powders

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Abstract

In this paper, high purity $BaTiO_3$ (BT) nano-powders with various grain sizes of 30–85 nm synthesized by chemical method were used to fabricate temperature-stable BT-based ceramic materials for application in base metal electrode (BME) multilayer ceramic capacitors (MLCC). The effects of the initial grain sizes of BT nano-powders on the phase structures, microstructures and dielectric properties of the ceramics were investigated. The BT based MLCC ceramics with the average grain size less than 200 nm were achieved in reducing atmospheres, showing high dielectric constant up to 2000, low dielectric loss less than 1%, which could satisfy the X7R characteristics prescribed by EIA standard.

Keywords: B. Grain size; B. Microstructure; C. Dielectric properties; D. $BaTiO_3$; E. Capacitors

1. Introduction

Conventional multilayer ceramic capacitors (MLCC) of X7R specification (a low dissipation factor of 2.5% or less, temperature coefficient of capacitance (TCC) within the range of ±15% between −55 and 125 °C) based on $BaTiO_3$ (BT) have been fabricated with electrodes of noble metals such as Pt or Pd. These electrodes are very expensive, although they are stable. To solve the problem, base metal such as Ni has been used as internal and external electrodes to replace the noble metals in MLCC, which can significantly reduce the production costs [1,2]. In this case, the dielectric materials must be fired in a low-oxygen partial pressure to prevent Ni from oxidizing. Many studies have been made on the additions such as MgO, MnO_2 and LiO–SiO_2–CaO, etc. [3] in preventing the material from reducing and controlling the temperature dependency of the dielectric constant. Incorporation behavior of co-doped rare-earth and acceptor elements was also studied [4]. With further developments in electronics, the miniaturization of electronic parts has proceeded quickly and the desire to increase the capacity of MLCC has also become more and more remarkable [5,6]. The thickness of the active layer has been reduced to satisfy these requirements. However, when the thickness of the dielectric layer in the monolithic ceramic capacitor becomes as thin as 2 μm, the grain size of ceramic grains in each layer should be reduced to 200 nm or less to meet the reliability requirement. Therefore, how to control the grain size in order to cope with thinning the layer thickness is still a challenge. To our knowledge, there are few papers concerning about fabricating MLCC ceramics using nanometer-sized BT powders.

In this study, BT nano-powders prepared by a chemical method were used to manufacture X7R-type temperature stable ceramic materials. The effects of the grain size, the modifier and sintering temperature on the microstructures and dielectric properties of the sintered ceramics were investigated.

2. Experimental procedure

The nano-sized powders of BT were synthesized by wet chemical method—oxalate precipitation method. The starting materials used in this study were barium acetate ($Ba(CH_3COO)_2$), tetrabutyl titanate ($Ti(OC_4H_9)_4$), oxalic

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acid ($H_2C_2O_4$) as precipitator and alcohol as a media solution. First, the oxalic acid was dissolved in alcohol, and tetrabutyl titanate was added into it with constant stirring to form a transparent yellow solution ($H_2TiO(C_2O_4)_2$). After that, the barium acetate solution were mixed with the above solution, ultrafine oxalate precipitate ($BaTiO(C_2O_4)_2{\cdot}4H_2O$) was obtained. The mole ratio of barium acetate, tetrabutyl titanate and oxalic acid used here was 1:1:2.2. The precursor was then dried and calcined at 750, 800 and 850 °C for 2 h to produce pure BT powders.

The obtained pure BT nano-powders were in cubic phases with the average grain sizes of 30, 50 and 85 nm, respectively. The additives MgO, MnO_2 and rare earth oxides Ho_2O_3 used here were of regent grade purity. Appropriate mixtures of the additives were pre-milled, mixed with BT powders and then milled, dried, pressed into disc-shaped form, and then sintered at 1200–1300 °C for 2 h in reducing atmospheres (97%N_2/3%H_2) followed by annealing in a weak oxidizing atmosphere at 1000 °C for 3 h.

The crystalline structures were investigated using X-ray diffraction (XRD Rigaku D/Max B). The microstructures of the ceramics were observed by scanning electron microscopy (SEM JEOL JSM6301F). The dielectric properties were measured using HP 4194A LF impedance analyzer over a temperature range from −60 to 150 °C at 1 kHz and 1 V_{rms}.

3. Results and discussion

3.1. Characteristics of BT nano-powders

Fig. 1a–c show the TEM images of BT powders calcined at different temperatures. It is obvious that the grain size increases with increasing calcining temperature. The crystalline structures were determined by XRD and the size-induced phase transition has been observed in this study. When the grain size is smaller than 85 nm, the BT powders are of cubic perovskite structures (paraelectric phase).

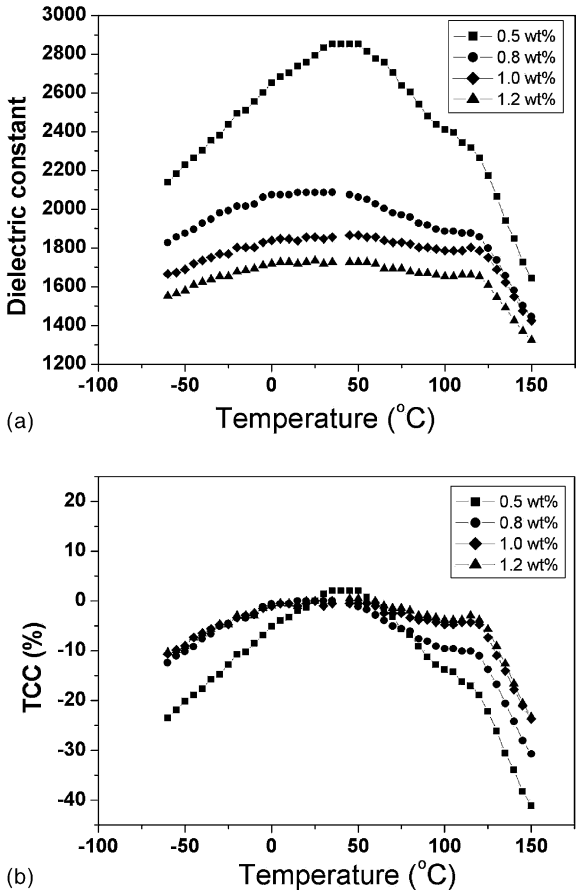

Fig. 2. The dielectric constant vs. temperature (a), TCC vs. temperature (b) for $BaTiO_3$-based ceramics with various amounts of Ho_2O_3 sintered at 1200 °C.

3.2. The influences of rare-earth oxide (Ho_2O_3)

BT powders with the average grain size of 85 nm were mixed with MgO (1 wt.%), MnO_2 (0.5 wt.%) and different amounts of Ho_2O_3 (0.5, 0.8, 1.0 and 1.2 wt.%) and sintered at 1200 °C. Fig. 2 shows the dielectric–temperature

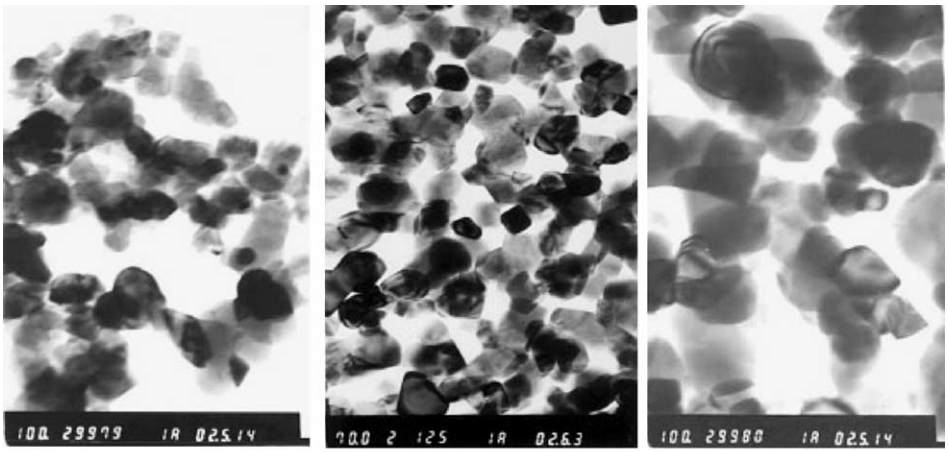

Fig. 1. SEM images of the $BaTiO_3$ powders with the grain size of (a) 30 nm; (b) 50 nm; (c) 85 nm.

characteristics of BT ceramics with various amount of Ho_2O_3. It can be found that the dielectric properties are strongly correlated with the rare-earth oxide concentration. Doped with 0.5 wt.% of Ho_2O_3, the ceramic exhibits a high dielectric peak around 40 °C, and the TCC value above 25 °C decreases to nearly −30%. With increasing Ho_2O_3 content, the TCC curve is flattened as shown in Fig. 2b, although the dielectric constant decreases. Only when the amount of Ho_2O_3 additive is above 1.0 wt.%, the TCC could satisfy the X7R specification. This result is consistent with the other studies reported by Kishi et al. [2]. As well known, the structure of X7R type ceramics consist two parts, the 'core' consisting of pure BT and showing ferroelectric properties, and the 'shell' containing non-ferroelectric materials, which is responsible for the dielectric–temperature characteristics of X7R ceramics. In the ceramics with low content of Ho_2O_3, Ho ions tend to occupy A-sites in the perovskite structure to form a solid solution characterized by the appear of large grains observed by SEM, other than to form the 'core-shell' structure, so the TCC change is very large. With the increase in Ho_2O_3 concentration, the stable core-shell structure could be formed and TCC curve becomes flattened. Considering both effect on the dielectric constant and TCC value, the optimum concentration of the rare earth oxide additive was 1.0 wt.% for preparing X7R type ceramic materials with high dielectric constant.

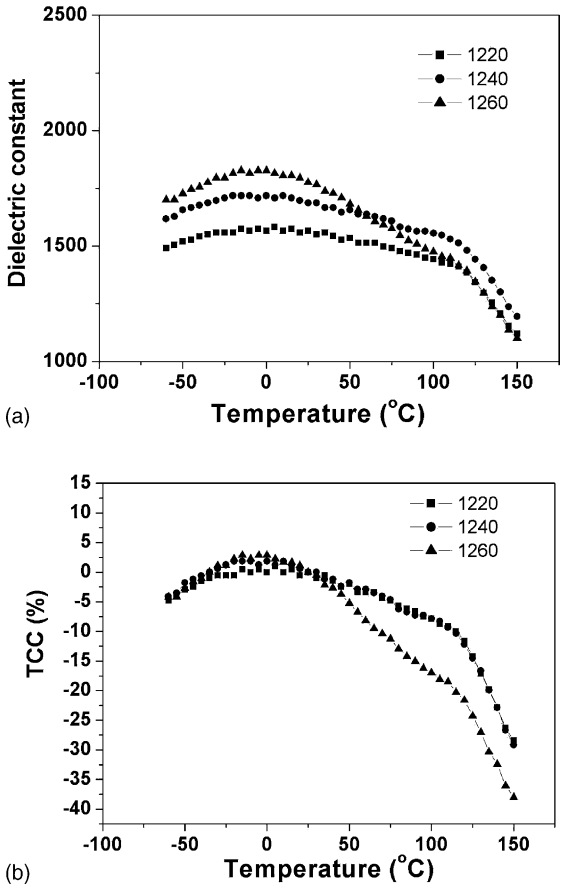

Fig. 3. The dielectric constant vs. temperature (a), TCC vs. temperature (b) for $BaTiO_3$-based ceramics with the initial grain size of 30 nm.

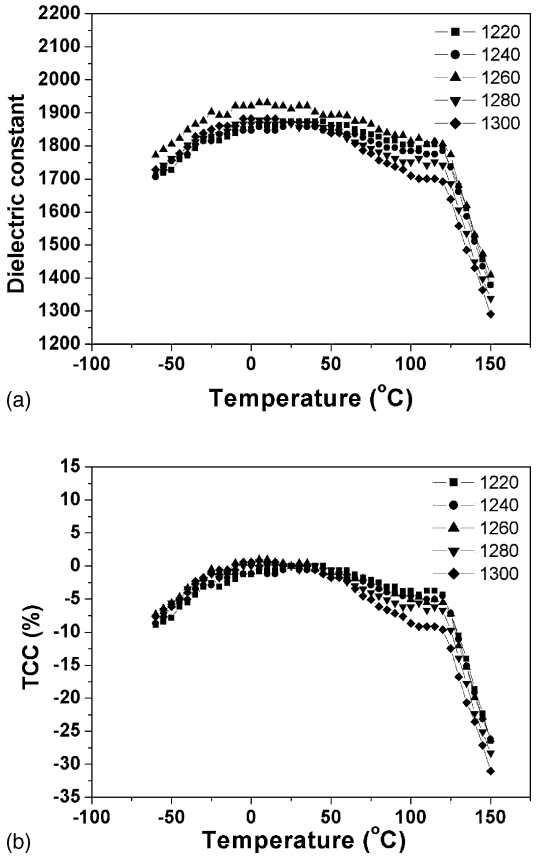

Fig. 4. The dielectric constant vs. temperature (a), TCC vs. temperature (b) for $BaTiO_3$-based ceramics with the initial grain size of 85 nm.

3.3. The effect of the initial particle size of BT

Figs. 3 and 4 show the dielectric–temperature characteristics of the BT-based ceramics with the same composition (1.0 wt.% Ho_2O_3) prepared from BT powders with different grain sizes of 30 and 85 nm, respectively.

For the samples derived from 30 nm BT powder, the dielectric properties could meet the requirement of X7R standards when sintered below 1240 °C, but the dielectric constants at 25 °C are relatively low (1600–1700). In addition, when sintering temperature increases to 1260 °C, the TCC above 25 °C drops to −25%, which indicates the core-shell structure is unstable in this case.

For the samples derived from 85 nm BT powder, the dielectric–temperature characteristics could satisfy the X7R specification for all the ceramics sintered at relatively wide temperature range of 1220–1300 °C with large dielectric constant of 1800–1950 at 25 °C. The larger the initial grain size of the powder is, the higher the dielectric constant has been achieved.

Fig. 5 shows the surface microstructures of the samples with different initial grain sizes. The ceramic grains show

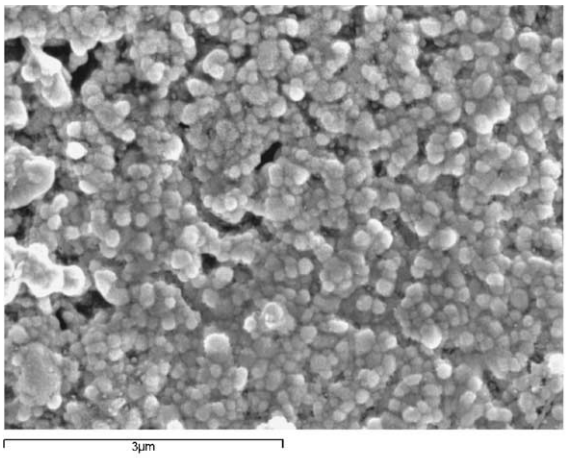

Fig. 5. SEM images of the $BaTiO_3$-based ceramics prepared from nano-powders with the initial grain sizes of (a) 30 nm; (b) 85 nm.

relatively uniform, and the average grain sizes are 110 and 150 nm for the ceramic samples with initial grain size of 30 and 85 nm, respectively.

The influence of the initial grain size upon the dielectric constant of the BT based ceramics may be attributed to the size effect of BT as reported in our previous paper [7]. The effect of ferroelectric BT, the 'core,' plays an important role on the dielectric properties, therefore, the increase in the grain size results in distinct enhancement of the dielectric constant. Furthermore, it can be concluded that the 'core-shell' structure formed in large-grained ceramics is more stable than that formed in the small-grained ceramics.

Being fully dense and ultrafine-grained microstructure, the ceramics are of high insulation resistivity above $10^{13}\ \Omega$ cm, low dielectric loss less than 1% and high standing voltage more than 10 kV/mm.

4. Conclusions

Using nanometer BT powders synthesized by a chemical method, X7R-type BT-based ceramic materials with grain size less than 200 nm were achieved for application in base metal electrode (BME) multilayer ceramic capacitors. The initial particle size, modifier amount as well as the sintering temperature affect the microstructures as well as the dielectric properties of the ceramics. The X7R type ceramics with the grain size of 150 nm exhibited high dielectric constant up to 2000 and high insulation resisitivity above $10^{13}\ \Omega$ cm. Therefore, this non-reducing ultra-fine grained ceramic material can be used for manufacturing ultra-thin-layered BME-MLCC.

Acknowledgements

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