

Modeling of the core-shell microstructure of temperature-stable BaTiO₃ based dielectrics for multilayer ceramic capacitors

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Abstract A simplified model was proposed for the core-shell microstructure, which existed in the temperature-stable BaTiO₃ (BT) based dielectrics for multilayer ceramic capacitors (MLCCs) and was regarded as the reason resulting in the temperature-stable characteristics. In this model the capacitance of a core-shell grain can be regarded as the parallel combination of the capacitance of the grain core and the grain shell. To verify the validity of the model, core material, shell material and core-shell material were prepared. Based on our previous work, BT with a grain size of 400 nm was chosen as the core material; X7R material milled for 1 hour was chosen as the core-shell material; doped BT milled for 36 h was chosen as the shell material. The calculated results showed good agreement with the measured experimental results of the core-shell material, which proved the validity of the model.

Keywords Barium titanate · Core-shell microstructure · Multilayer ceramic capacitors · X7R · Modeling

1 Introduction

During the past decade, with the rapid development of the electronic industry, multilayer ceramic capacitors (MLCCs) have been widely used in many electronic devices, because of their properties of high capacitance with small sizes, high reliability and excellent high-frequency characteristics

[1–3]. Driven by the enormous market demands, there is an increasing need for the temperature-stable materials for the manufacture of MLCCs that meet the specification of X7R in the Electronic Industries Association (EIA) standard, which demands the dielectric constant of the materials does not change by more than 15% from its 25 °C value over the temperature range of from –55 to +125 °C. In order to produce the required temperature-stable characteristics of X7R materials, pure BaTiO₃ (BT) must be modified chemically and physically [4]. A so-called core-shell microstructure is observed in these materials resulting from donors and acceptors doping, which has been proved to result in the temperature-stable characteristics. In the chemical inhomogeneity core-shell microstructure, the grain core is ferroelectric of pure BT while the grain shell is paraelectric of doped BT [5, 6]. Thus the flat high-dielectric-constant temperature characteristics can be associated with the high dielectric constant of the grain core in the high-temperature regions and of the grain shell in the low-temperature regions [7, 8].

Many researches have been reported on the formation mechanism or microstructure observation of the core-shell microstructure [9–14]. However few has been focused on modeling the core-shell microstructure except for D. Hennings who proposed a semi-quantitatively Lichtenecker formula [9, 15]:

$$\log \varepsilon = V_1 \bullet \log \varepsilon_1 + V_2 \bullet \log \varepsilon_2 \quad (1)$$

where V_1 , V_2 and ε_1 , ε_2 are the respective volume fractions and relative dielectric constants of the materials in core and shell.

In this study we provided a simplified model for the core-shell microstructure. Moreover the core material, shell material and the core-shell material were prepared as well to verify the validity of this model.

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Table 1 Experimental compositions, milling condition, and sintering conditions.

Sample	Composition (wt)	Milling time (h)	Sintering condition
A1	10BT+0.05Y ₂ O ₃ +0.04MgO+0.02MnO ₂ +0.03SiO ₂	1	1250 °C/2 h
B1	10BT+0.15Y ₂ O ₃ +0.12MgO+0.06MnO ₂ +0.09SiO ₂	36	1250 °C/2 h
B2	10BT+0.09Y ₂ O ₃ +0.07MgO+0.03MnO ₂ +0.05SiO ₂	36	1250 °C/2 h
B3	10BT+0.07Y ₂ O ₃ +0.06MgO+0.03MnO ₂ +0.04SiO ₂	36	1250 °C/2 h
B4	10BT+0.05Y ₂ O ₃ +0.04MgO+0.02MnO ₂ +0.03SiO ₂	36	1250 °C/2 h

2 Experimental procedure

The original pure BT powder was GuoTeng's electronic grade product synthesized hydrothermally with a grain size of 100 nm. The powder was calcined at 1000 °C for 2 h, and the grain size grew up to about 350 nm. All the additives (Y₂O₃, MgO, MnO₂ and SiO₂) used here were of reagent grade purity. The calcined BT powder and the additives were mixed by ball milling for different time. The medium used in the milling process is ZrO₂ beads with a diameter of 3 mm, whose weight was 15 times that of the BT powder. The powder mixtures were subsequently dried and pressed into disks with about 10 mm in diameter and 1 mm in thickness, then sintered at 1250 °C for 2 h in a reducing atmosphere, followed by a reoxidization process at 1000 °C for 3 h. The densities of the sintered ceramics exceeded 5.7 g/cm³. The experimental details are described in Table 1.

The temperature dependence of the dielectric constant at 1 kHz was measured at 1 V_{rms} by HP 4192A LF impedance analyzer. Foils for transmission electron microscopy (TEM JEM-2010F) analysis were prepared by grinding samples to a thickness of 30 μm and ion-beam thinning to perforation. The transmission electron microscope was operated at 200 kV, and energy dispersive spectroscopy (EDS) microanalysis was performed.

3 Results and discussion

Figure 1(a) presents a TEM micrograph of typical core-shell microstructure, based on which a simplified model that neglects the concentration gradient in the grain shell is proposed in Fig. 1(b). In this model, a core-shell grain is considered as an ideal sphere, in the center of which is a spherical pure BT core enwrapped by a doped BT shell. According to this model, the resultant capacitance of the grain can be considered as the parallel combination of the two parts, the grain core and the grain shell. The capacitance of the grain core is

$$C_c = 4\pi\epsilon_c r_c \quad (2)$$

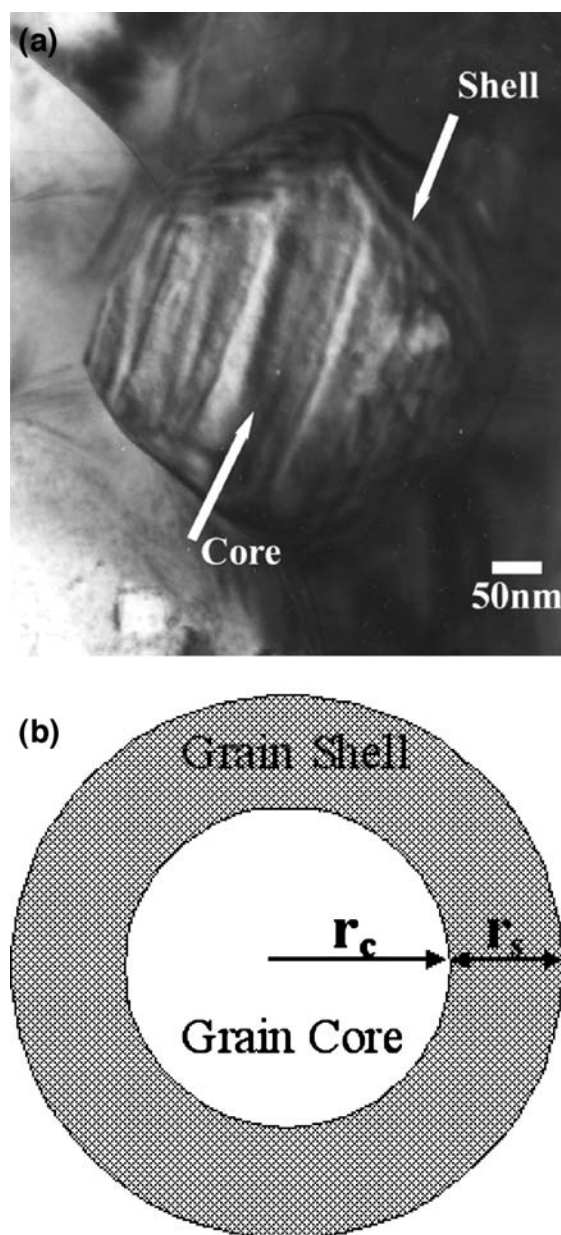


Fig. 1 (a) TEM micrograph of typical core-shell microstructure; (b) Modeling for the core-shell microstructure consisted of parallel combination of grain core and grain shell

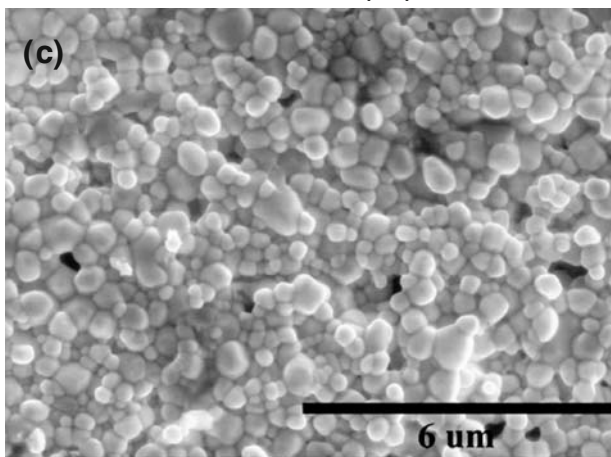
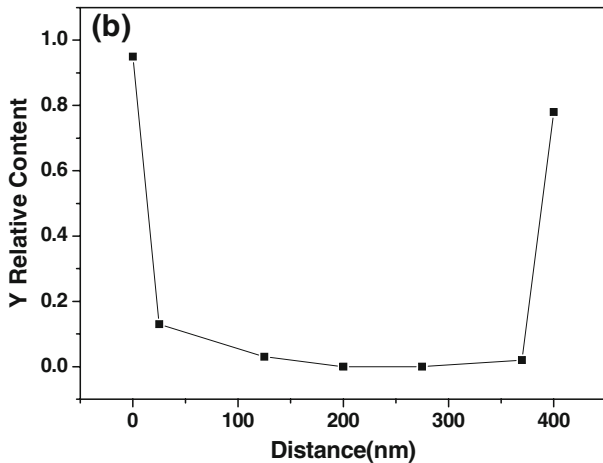
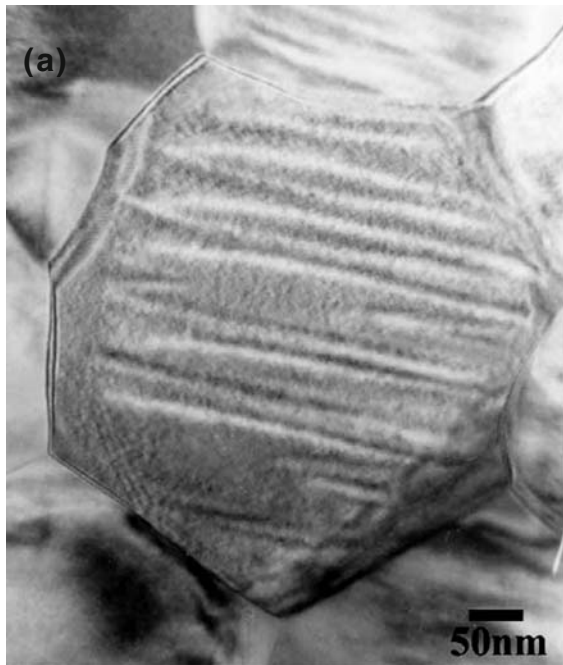


Fig. 2 (a) TEM observation of the core-shell microstructure of sample A1 milled for 1 h; (b) EDS analysis for Yttrium in the core-shell microstructure; (c) SEM surface micrograph for sample A1 with grain size of 400 nm

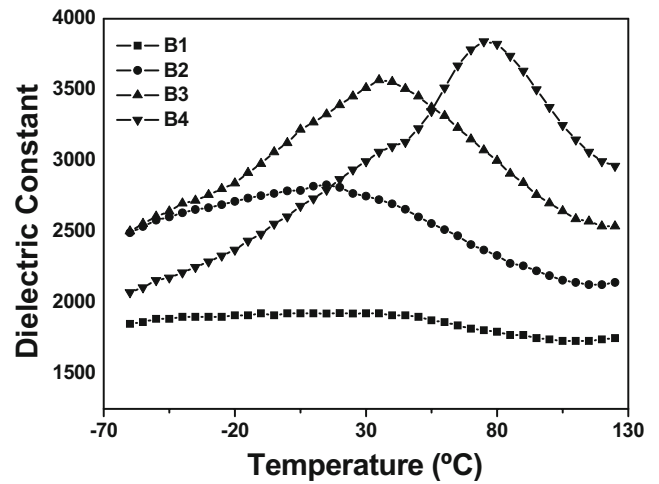


Fig. 3 Dielectric properties of shell materials with various additive concentration (wt%): B1—4.2%; B2—2.4%; B3—2.0%; B4—1.4%

where ϵ_c and r_c are the dielectric constant and radius of the grain core, respectively. The capacitance of the grain shell is given as

$$C_s = \frac{4\pi\epsilon_s r_c (r_s + r_c)}{r_s} \quad (3)$$

where ϵ_s and r_s are the dielectric constant and thickness of the grain shell, respectively. The parallel combination of the two parts should be

$$C_g = \frac{1}{\frac{1}{C_s} + \frac{1}{C_c}} \quad (4)$$

Furthermore the capacitance can also be calculated by the following expression

$$C_g = 4\pi\epsilon_g (r_s + r_c) \quad (5)$$

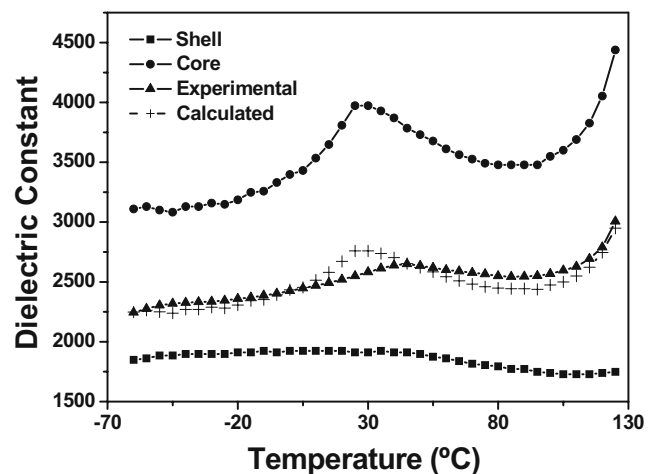


Fig. 4 Simulated dielectric constant-temperature curve of core-shell structured materials (shell material—sample B1; core material—BT with a grain size of 400 nm; core-shell material—sample A1)

where ε_g is the dielectric constant of the core-shell grain. Therefore according to Eqs. 2~5, the dielectric constant of the grain can be expressed by the following equation:

$$\varepsilon_g = \frac{\varepsilon_c \varepsilon_s r_c}{\varepsilon_s (r_s + r_c) + \varepsilon_c r_s} \quad (6)$$

In order to verify the validity of the model and Eq. 6, it is necessary to compare the simulate result with the experimental curve. In another work, we have found that milling process has a great influence on the core-shell microstructure, which can be used to control the core/shell ratio. In this paper we choose sample A1 as the core-shell material which has been milled for 1 h and exhibits a shell thickness of 25 nm, as displayed in Fig. 2(a) and (b). Fig. 2(c) reveals that the grain size of the core-shell material is about 400 nm.

As we have reported, when the milling time is long enough, the additives will spread the whole grain, which leads to the collapse of the core-shell microstructure and formation of a chemical homogeneous solid solution. This solid solution exhibits similar characteristics with the grain shell. Thus we prepared four samples B1–B4 as the shell materials which have been milled for 36 h. The dielectric properties of sample B1–B4 are presented in Fig. 3. As the figure shows, the dielectric constant-temperature curve becomes flat and the Curie peak moves towards low-temperature regions with the increasing additive concentration, which will explain why the grain shells exhibit paraelectric at room temperature. When the grain shell contains an enough high additive concentration, the Curie peak will move toward below room temperature, consequently the shell will show paraelectric at room temperature.

Since the additive concentration in grain shell of the core-shell material (A1) is:

$$C_{\text{shell}} = \frac{C_{\text{grain}}}{V_{\text{shell}}\%} \frac{1.4\%}{1 - \frac{\frac{4}{3}\pi(175\text{nm})^3}{\frac{4}{3}\pi(200\text{nm})^3}} = 4.2\% \quad (7)$$

which is equal to the concentration of sample B1, in our following simulation, sample B1 is chosen as the shell material. Moreover as was reported, the dielectric properties of BT exhibits distinct size effect [16], pure BT with a grain size of 400 nm is chosen as the core material to simulate the dielectric properties of the grain core. The calculated and experimental results are shown in Fig. 4. As the figure reveals, the results show that the simulated results calculated from Eq. 6 agree with the measured curve of core-shell material quite well, which supports the validity of the model shown in Fig. 1 and Eq. 6.

However, since the model neglects the concentration gradient in the grain shell and the size effect on the

dielectric properties of the shell, which is very weak and can be neglected in a thinner grain shell but quite influential and can not be neglected as the shell gets thicker, the model will be quite valid in the grains with thin shells, but not very suitable for those with thick shells. More efforts will be focused on a modified model suitable for grains with thick shells in the future work.

4 Conclusions

A simplified model for the core-shell microstructure was proposed. The capacitance of a core-shell grain can be regarded as the parallel combination of the capacitance of the grain core and the grain shell. To verify the validity of the model, core material, shell material and core-shell material were prepared. BT with a grain size of 400 nm was chosen as the core material; X7R material milled for 1 hour was chosen as the core-shell structured material; doped BT milled for 36 h was chosen as the shell material. The results show that the simulated results calculated from the model agree with the measured curve of core-shell material quite well. However the model was not very suitable for the grains with thick shells.

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