Dimension effects on the dielectric properties of fine $BaTiO_3$ ceramics*

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It is found that the core-shell structured grains are easy to produce for fine grain doped $BaTiO_3$ ceramics in the sintering process. We study the influence of the core-shell structure on the Curie–Weiss temperature and dielectric properties of $BaTiO_3$ ceramics by using effective medium approximation (EMA). Considering the second approximation, the dielectric properties of fine grain doped $BaTiO_3$ ceramics are consistent with experimental data.

Keywords: core-shell structure, Curie–Weiss temperature, $BaTiO_3$ ceramics, second approximation

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1. Introduction

$BaTiO_3$ ceramics is one of the most important dielectric materials that have been used widely in various fields. The performances of $BaTiO_3$ ceramics can be changed and improved through the addition of different dopants in order to meet the special application. However, it is very easy to result in core-shell structured grains after sintering,[1–5] due to the solid solution of dopants in the grain boundary and diffusion of dopants to the interior of the grain. Grain growth could be inhibited due to the drag effect caused by the dopant atoms distributing on the outer layer of the grain.[6,7] It has been suggested that the drag force is proportional to the difference between dopant atom concentrations in the grain exterior region and in the interior region.[8–11]

It is proved that the core is nearly free from dopants and retains as a ferroelectric phase, while the shell is a paraelectric phase. Therefore, the effective dielectric properties of $BaTiO_3$ grains are dependent on the volume fractions of core and shell. However, for pure $BaTiO_3$ ceramics, a 'dead' surface layer of grain can appear, which is different not only to the interior of a grain but also to the grain boundary. In this case, the grain can also be seen as a core-shell structure when the effects of the surface layer are taken into account.

It is well known that the dielectric constant decreases with reducing grain size (GS) for fine grains (GS < 1 μm) ceramics. The grain size is controlled not only by the particle size of the powder but also by the process of sintering. It is comprehensible that the reduction of grain size may increase the volume fractions of shell, which can influence the dielectric properties of ceramics.

In this paper, using EMA theory, the dielectric constant of the equivalent three components composite system for spherical grain is analyzed. The dimension effects on the dielectric constant are also discussed for fine $BaTiO_3$.

2. Theoretical consideration

The shape of grain changes to be more symmetrical and approximately spherical with the decrease of grain size. To apply this method, the following assumptions are made: (i) fine grain is spherical and has a core-shell structure, (see Fig. 1); (ii) the ceramics can be seen as a random mixed system of spherical grain (including core and shell) and grain boundary materials;[12,13] (iii) the mixed system has a microstructure of statistical equivalence.

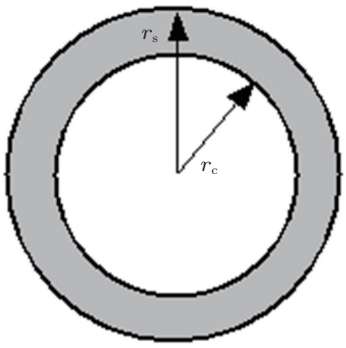


Fig. 1. Core-shell structure of grains.

Supposing that the conductivity and radius of core and shell are (σ_c, r_c) and (σ_s, r_s) respectively. The σ_b, ε_b, and r_b is the conductivity, relative dielectric constant, and average thickness of material around the grain, respectively. It is convenient to calculate by importing a structure parameter β, which is equal to r_c/r_s.

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The distribution of potential in grain can be found by solving Laplace's equation when there is an external electric field.[11] The polarization of spherical grain induced by an external electric field can be depicted by the following formula when $\sigma_s = \eta\sigma_c$:

$$P = E_0 r_s^3 \frac{\mu\sigma_c - \sigma_b}{\mu\sigma_c + 2\sigma_b}. \tag{1}$$

Thereby, the relative dielectric constant of ceramic grains can be written as

$$\varepsilon_r = \frac{1}{\varepsilon_0} r_s^3 \frac{\mu\sigma_c - \sigma_b}{\mu\sigma_c + 2\sigma_b} + 1, \tag{2}$$

where E_0 is the external electric field, ε_0 is the vaccum dielectric constant, and

$$\mu = \frac{\eta(1+2\eta) + 2\beta\eta(1-\eta)}{(1+2\eta) - \beta(1-\eta)}. \tag{3}$$

Since

$$\bar{\sigma}_c = \mu\sigma_c = \frac{\eta(1+2\eta) + 2\beta\eta(1-\eta)}{(1+2\eta) - \beta(1-\eta)}\sigma_c, \tag{4}$$

we can obtain the relative dielectric constant of ceramic grain as

$$\varepsilon_r = \frac{1}{\varepsilon_0} r_s^3 \frac{\mu\bar{\sigma}_c - \sigma_b}{\mu\bar{\sigma}_c + 2\sigma_b} + 1. \tag{5}$$

If the volume fraction of grain is V_1, then the total average dielectric constant can be given by[17,18]

$$\begin{aligned} &\varepsilon_s = F\varepsilon_r, \\ &F = \alpha + \left(\alpha^2 + \frac{1}{2}x\right)^{1/2}, \\ &\alpha = \frac{1}{4}\left[(3V_1 - 1)(1+x) + x\right], \\ &x = \frac{\varepsilon_b}{\varepsilon_r}. \end{aligned} \tag{6}$$

The distribution of additional concentration can be depicted by the error function

$$\begin{aligned} &c(x,t) = c_0\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right], \\ &\text{where } \mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \mathrm{e}^{-\lambda^2}\,\mathrm{d}\lambda. \end{aligned} \tag{7}$$

The exchange or homogenization is nearly completed for a sphere when diffusion distance (x) meets the following relation:

$$x = \sqrt{Dt} = 0.75 r_c. \tag{8}$$

We suppose that $D = 6.31 \times 10^{-5}\exp(-4.55/kT)$, for $r_c = 100$ nm, the ideal diffusing time can be obtained from formula (8). It is about 140000 s (39 h), but the real sintering time in experiments is about 1 h. Thus, the diffusion distance (shell thickness) is

$$x \approx 0.12 r_c. \tag{9}$$

In our experiments, the shell thickness was measured for samples of different GS for doped $BaTiO_3$ ceramics. The results are compared with the one calculated from formula (9) (see Fig. 2).

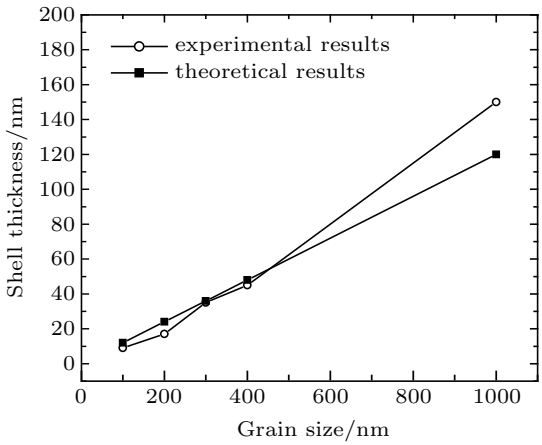


Fig. 2. Shell thickness as a function of grain size.

There are differences between experimental and theoretical results for grain size greater than 500 nm, which may be due to the insufficiency of spherical grain for large grain. It is shown that the theoretical results conform to experimental ones. Thus, the geometry factor β ($= r_c/r_s = r_c/(r_c + x)$) is about 0.9.

Synthesizing the above analysis, the relative dielectric constant of grain, which is related to the properties of grain, grain boundary materials, and the sintering condition, can be derived by combining Eqs. (5), (6), and (9), that is,

$$\varepsilon_s = F\frac{1}{\varepsilon_0}\left(\frac{r_c}{\beta}\right)^3 \frac{\mu\bar{\sigma}_c - \sigma_b}{\mu\bar{\sigma}_c + 2\sigma_b} + 1. \tag{10}$$

3. Discussion

It is obvious that the volume fraction V_1 of grains decrease with reducing grain size, which is approximately proportional to $(1 - r_b/r_c)$, where r_b is the thickness of the grain boundary. Hence, α and F in Eq. (6) all decrease, which leads to the decrease of the relative dielectric constant. At the same time, the additional concentration on the boundary reduces because the area of the boundary surface increases with decreasing the grain size. Therefore, the diffusion distance (r_s) decreases. If the geometry factor β is constant, then the dielectric constant can be rewritten as

$$\varepsilon_s = K\left(1 - \frac{r_b}{r_c}\right)\frac{1}{\varepsilon_0}\left(\frac{r_c}{\beta}\right)^3 \frac{\mu\bar{\sigma}_c - \sigma_b}{\mu\bar{\sigma}_c + 2\sigma_b} + 1. \tag{11}$$

In order to investigate the changing trend of ε_s with the grain size r_c, formula (11) can be simplified into the following form when the equivalent conductivity is constant:

$$\varepsilon_s = K'\left(1 - \frac{r_b}{r_c}\right) r_c^3 + 1, \tag{12}$$

where K' is a simplifying coefficient. If K' is equal to 1, then the theoretical changing curve of formula (12) for different r_b are shown in Fig. 3.

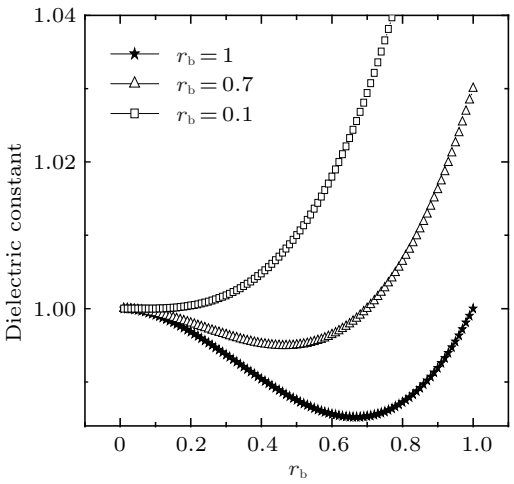


Fig. 3. Theoretical curves from formula (12).

It is shown from Fig. 3 that the dielectric constant decreases with increasing r_b, which reveals the influence of grain boundary. It is obvious that the increase in boundary thickness is disadvantageous for improving the dielectric properties.

Generally, K is a very large number. It can be gained empirically by adapting formula (12) to well-known experimental data. In Fig. 4, the dielectric constant calculated though formula (12) when $r_b = 2$ nm is compared to our experimental results.[19,20]

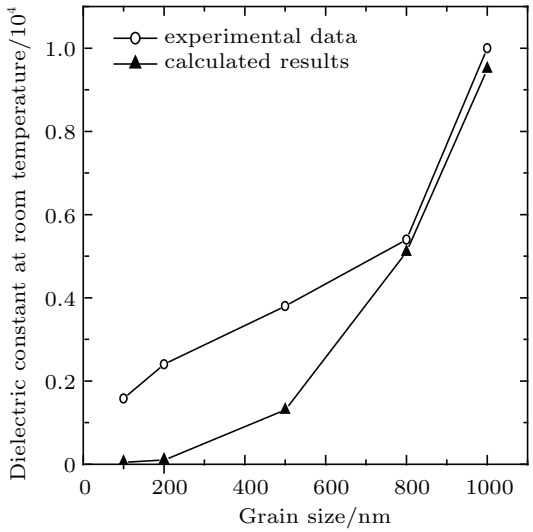


Fig. 4. Experimental and calculated results.

It is shown in Fig. 4 that the trends of two curves are similar. However, there are large differences at the small grain size. This is due to the assumption that the geometry factor β is a constant for grains of different size. Because the concentration of additions on the surfaces decreases due to the increase in grain surfaces when the grain size decreases, the size of shell does not change linearly with grain size. Thereby, β may not keep constant. On the other hand, the equivalent conductivity decreases generally with grain size, which may also influence the calculated results.

In Fig. 3, it is worth noting that the dielectric constant begins to increase when the thickness of the grain boundary increases and GS reduces to a certain value. This result is in good consistence with the experimental results reported on nanocrystalline $BaTiO_3$ ceramics.[20,21]

The renormalized Curie–Weiss temperature can also be obtained by Eqs. (1)–(3)[22] based on the core-shell structure, which is approximately depicted as follows:

$$T^* = T_0 - \frac{C}{\varepsilon_b} \frac{r_c^3 - (r_c - 2d)^3}{2r_c^3 + (r_c - 2d)^3}, \tag{13}$$

where T^* is the renormalized effective Curie–Weiss temperature; T_0 and C are the Curie–Weiss temperature and the Curie–Weiss constant of single crystal, respectively; and d is the thickness of the grain boundary.

In general, $d << r_c$, so formula (13) can be expanded by series. In second approximation, formula (13) can be simplified into the following relation:

$$T^* = T_0 - \frac{C}{3\varepsilon_b}\left[\frac{6d}{r_c} - \frac{12d^2}{r_c^2}\right]. \tag{14}$$

Since

$$(T^*)'_d = \left[T_0 - \frac{C}{3\varepsilon_b}\left(\frac{6d}{r_c} - \frac{12d^2}{r_c^2}\right)\right]'_d = 0, \tag{15}$$

we have

$$4d = r_c. \tag{16}$$

By selecting reasonable parameters, such as $C = 1.8 \times 105$, $\varepsilon_b = 80$, $d = 2$–3 nm and $T = 125$ °C, T^* can be calculated. T^* decreases with reducing GS, which has the same changing trend as the Curie temperature measured in our experiments for fine ceramics (see Fig. 5).

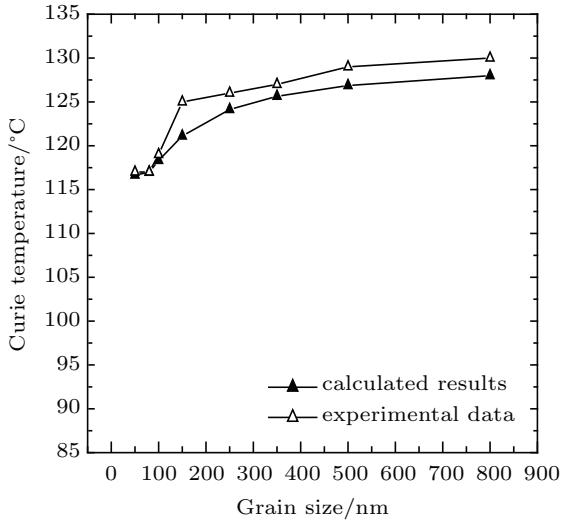


Fig. 5. Apparent Curie–Weiss temperature as a function of grain size.

It is shown from Eq. (15) that T^* has a minimum at certain GS, which indicates that the structure and properties of grains change remarkably. This GS may be seen as a critical grain size. We can see from formula (16) that it is about 8–12 nm when the thickness of grain boundary d is 2–3 nm. This result is similar to other experimental predictions.[23,24]

4. Conclusion

The dielectric properties of fine grain $BaTiO_3$ ceramics are studied theoretically based on the core-shell structure of grains. The theoretical results are gained by using the effective medium approximation (EMA) theory. It is shown that theoretical results agree with the experimental observation. It is revealed that the core-shell structure of grains has a certain influence on the dielectric properties of ceramics. The thickness of the shell is proportional to the grain size. The dielectric constant of the fine grain ceramics may decrease when the thickness of the shell increases. The Curie–Weiss temperature does not decrease continuously with reducing the grain size. There is a critical size of grain, at which the Curie temperature is minimum, i.e., about 10 nm.

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