Ceramics International 25 (1999) 727–729

CERAMICS INTERNATIONAL

Size effect on dielectric properties of fine-grained $BaTiO_3$ ceramics

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Received 21 July 1998; received in revised form 5 October 1998; accepted 7 December 1998

Abstract

The effect of grain size on the dielectric behavior of high-purity, fine-grained $BaTiO_3$ ceramic has been investigated. It was found that the dielectric constant and dissipation factor changed much with the decreasing of average grain size. The specimen with grain size of 280 nm had a high dielectric constant at room temperature, and the $\varepsilon_r - T$ and $\tan\delta - T$ curves remarkably changed with the grain size. Part of the grains remaining ferroelectric structure was ascribed to the high value of dielectric constant.

Keywords: B. Grain size; C. Electric properties; D. $BaTiO_3$

1. Introduction

The study of size effect in ferroelectric systems has lately become very important because of their potential applications. It was found that the dielectric properties of $BaTiO_3$ ceramic strongly depend on its grain size. Coarse-grained ceramics of pure $BaTiO_3$ (20–50 μm) show $\varepsilon_r \approx 1500$–2000 at room temperature [1]. A pronounced maximum $\varepsilon_r \approx 5000$ at grain size 0.8–1 μm was found [2]. At even smaller grain sizes, a strong decrease of ε_r was observed. Many authors considered that when the grain size is lower than 700 nm, the lattice of $BaTiO_3$ ceramic changes from tetragonal to pseudocubic, and the dielectric constant value is very low [3–5].

However, there appears to be no definitive report of the measurement and interpretation of the dielectric response function in fine-grained ferroelectric systems, since a dense microstructure with superfine grain size is difficult to obtain. Some additives have been reported to effectively prevent discontinuous grain growth, but when the physical properties are the most stringent, they should be avoided. The objective of this paper is to investigate the grain size effect on the dielectric properties of fine-grained $BaTiO_3$ without dopants.

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2. Experimental

To fabricate fine microstructure $BaTiO_3$ ceramics with high density, a high-purity, stoichiometric, well-distributed $BaTiO_3$ powder with average grain size of 13 nm of cubic symmetry was prepared by a modified sol-gel method using hydroxide and alcoholate as precursors. The powders were hot pressed in vacuum at 1050–1150°C at aniaxial pressures of about 30 MPa. For electrical measurements, conducting silver paste was coated and curved at 600°C for 30 min. The ceramic density was measured by Archimede's method. The average grain size was determined on thermally etched ceramics photographs of scanning electric microscope (SEM). The dielectric constant and dissipation factor were measured by a Hewlett–Packard 4192A impedance analyser at temperature between room temperature and 180°C. At least three pellets were scanned for each sample corresponding to a particular size.

3. Results and discussion

It is difficult to prepare properly dense ceramics with superfine grain size, for a large strain is developed when the sample undergoes the cubic to tetragonal structural transition, which often leads to a crumbling of pellet. At the same time, with the decrease of grain size, the special

0272-8842/99/$ - see front matter
PII: S0272-8842(99)00009-7

surface energy increase much and then result in irregular growth with the increase of sintering temperature. To get fine-grained specimens with high density, many influent factors must be extensively studied, including the powder processing, the sintering condition, and so on.

In Fig. 1, we give the microstructures of specimens sintered at different temperatures. The average grain size and relative density are shown as Table 1.

It was found that both the density and grain size increase quickly with the increase of sintering temperature. After sintering at 1050°C, a dense specimen of fine grain size was obtained. Decreasing the sintering temperature, the grain size of specimen was finer, but the porosity became higher than that sintered at 1050°C, and these would distinctly affect the ceramic properties.

Fig. 2 shows the temperature dependence of the dielectric constant of $BaTiO_3$ with different grain sizes. It was found that the ε_{max} reduce to lower values and the peaks become increasingly flat with the lower grain size. The sample with an average grain size of 1800 nm has the highest dielectric constant of more than 6000, showing a sharp dielectric peak at 130°C. With the lower of grain size, the dielectric constants drop rapidly. For a sample with a size of 280 nm (sintered at 1050°C), a broad peak was observed in the transition area and a high dielectric constant of more than 3000 was obtained. The nature of the dielectric transition, therefore, shows change with the reduction of grain size.

The observed broadenings of the dielectric constant at the ferroelectric transition are typical of 'relaxor' materials which exhibit diffused phase transitions (DPT). The curie temperatures slightly shift to lower temperatures. It has been reported that when the grain size is smaller than 700 nm, 90° electric domains almost disappear and the lattice changes from tetragonal to pseudocubic, so the ε_{RT} of ceramic decreases sharply [3–5]. Low ε_r values with broad distribution at the transition region are considered to be the characteristic of these relaxor materials. However, we have a different result in our experiment. The ε_r values we got were above 3000. Even though the 280 nm specimen has a lower density ($93\%\rho_t$) comparing with those two larger grain specimens, the porosity is not an important parameter that affects the ε_r when the relative density is above $90\%\rho_t$ [6], hence the porosity effect can be ignored. The high value of ε_r we obtained cannot be explained with respect to the earlier theories [3–5]. The ceramic is of pure $BaTiO_3$ without any additives, so the chemical defects can be neglected, too. The high ε_r value can be ascribed to some grains still remaining tetragonal in structure. With the reduction of grain size, some grains change to pseudocubic. At the same time, the amount of interfaces increases and the effect of depolarization strengthens, which result in low dielectric constant. Because most of the grains remain a tetragonal ferroelectric structure, the value of the dielectric constant lowers a little. Analyzed from the result of our experiments, we believed that to the ceramics with grain size lower than 400 nm, both the grain surface and the grain structure determine the dielectric constant. This was different from the theory that only grain boundaries have effect on dielectric properties to ceramics finer than 400 nm.

Table 1
Parameters measured for differently prepared $BaTiO_3$

Specimens	No. 1	No. 2	No. 3
Sintering condition	1050°C 30 min	1100°C 30 min	1150°C 30min
Average grain size (nm)	280	760	1800
Relative density ($\%\rho_t$)	93.17	97.32	98.83

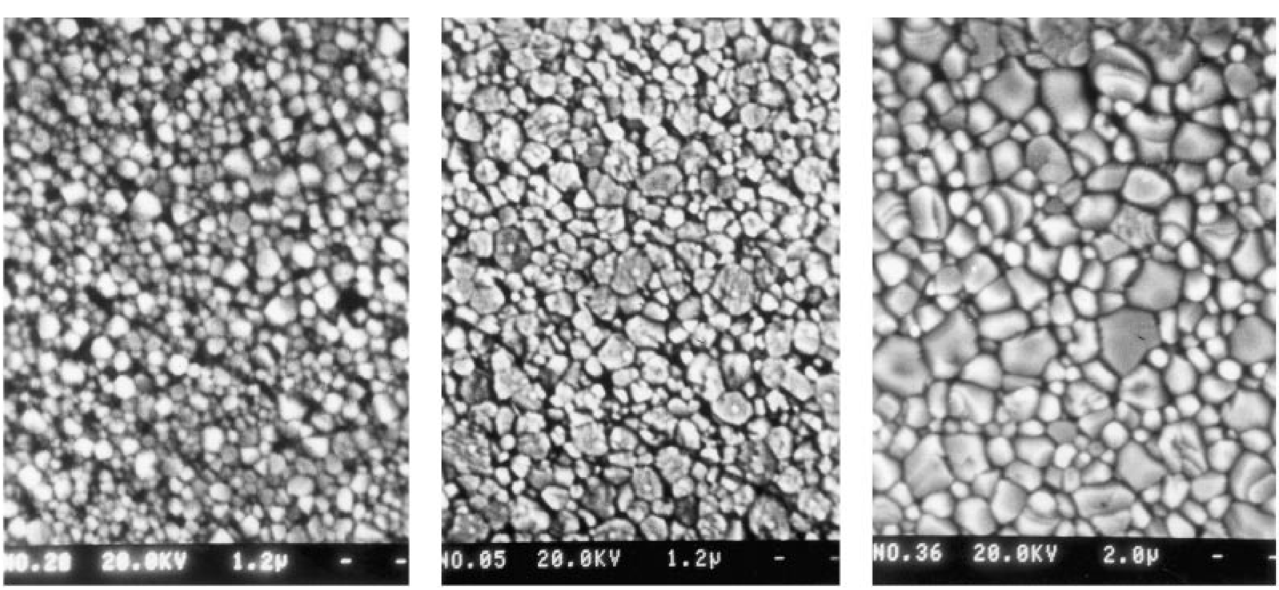

Fig. 1. Microphotographs of fine-grained $BaTiO_3$ after being thermally etched for 30 min in air.

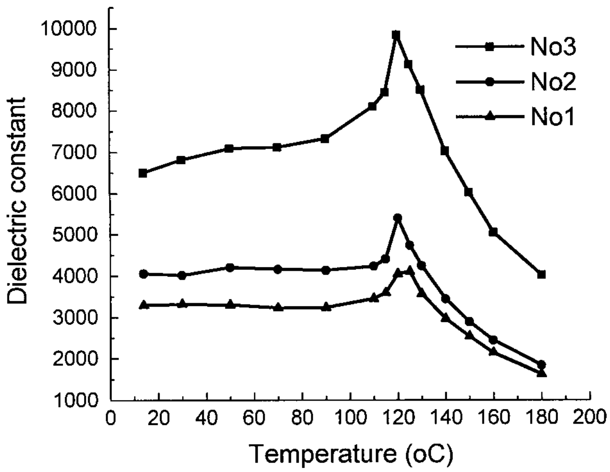

Fig. 2. Dielectric constant of $BaTiO_3$, sintered at different temperatures.

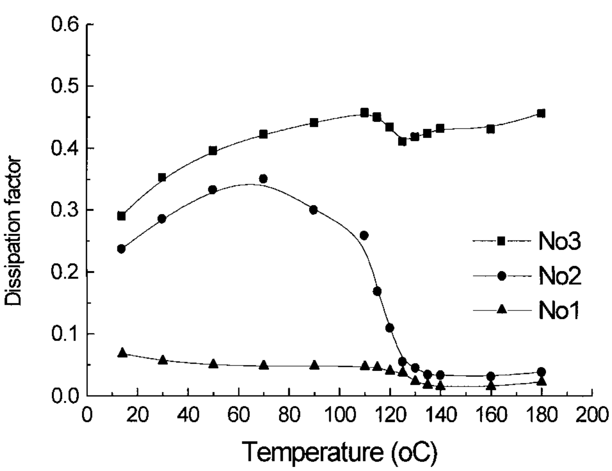

Fig. 3. Dissipation factor of $BaTiO_3$ sintered at different temperatures.

Recently, the determination of critical size of ferroelectric materials attract interests of many investigators. Since the difficulties of preparing fine-grained ceramics, these studies are limited in the theoretic discussion, which still need the proof of experiments.

Fig. 3 shows the temperature dependence of the dissipation factor of various grain size ceramics. When the grain size was 1800 nm, the specimen showed the highest value of dissipation factor, which slowly lowered with the rise of temperature. For the specimen of 760 nm, the dissipation factor attained a peak at 30°C and sharply decreased after it. When the grain size reduced to 280 nm, the dissipation factor was very low and gently dropped with the rise of temperature. The effect of grain size on dissipation factor can be ascribed to the change of microstructure. With the decrease of grain size, the transition rate of grains changing from tetragonal to pseudocubic increased and the degree of spontaneous polarisation decreased. So the energy needed for dipoles to revolve under the effect of electric field is lowered, then the dissipation factor is reduced. For the thermal vibration energy increases with the temperature, dipole revolving energy is much more lowered, thus resulting in the reduction of dissipation factor with the rise of temperature.

4. Conclusions

The dielectric properties of barium titanate ceramics were measured by changing the grain size between 280 nm and 1.8 μm. The observation confirmed that the dielectric properties are dependent on the grain size. When grain size reduced to 280 nm, a diffused phase transition were found. High dielectric constant value and low dissipation factor were observed in the specimen of 280 nm, which cannot be explained by earlier theories. Part of grains remain tetragonal structure is considered to be the cause. Further theoretical and experimental work are being done.

References

[1] N.C. Sharma, E.R. McCartney, J. Aus. Ceram. Soc. 10 (1974) 16–20.
[2] G. Arlt, H. Peusens, Ferro. 48 (1983) 213–224.
[3] G. Arlt, D. Hennings, G. With, J. Appl. Phys. 58 (1985) 1619–1625.
[4] A.S. Shaikh, R.W. Vest, G.M. Vest, IEEE Trans. Ultra. Ferro. and Freq. Contrl. 36 (1989) 407–412.
[5] S. Chattopadhyay, P. Ayyub, V.R. Palkar, M. Multani, Phys. Rev. B, 52 (1995) 13177–13183.
[6] T.T. Fang, H.L. Hsieh, F.S. Shiau, J. Am. Ceram. Soc. 76 (1993) 1205–1211.