

Relationship between Microstructure and Electrical Properties in Dielectric Ceramics with Core-Shell Structure

Hirokazu Chazono and Hiroshi Kishi

Taiyo Yuden Co., Ltd.

5607-2 Nakamuroda Haruna-machi, Gunma-gun, 370-3347, Japan

Fax: 81-027-360-8315, e-mail: hchazono@jty.yuden.co.jp

The microstructure and the electrical properties of multi-layer ceramic capacitors with Ni internal electrode (Ni-MLCCs) were investigated in BaTiO₃-MgO-Ho₂O₃ system. The dielectric constant increased as the firing temperature increased due to the microstructural evolution. Compositional analysis for Ni-MLCC samples fired at 1300°C using an analytical electron microscope revealed that the Ho concentration in the shell phase was not constant but showed a rather scattered distribution of the concentration. The temperature dependence of the dielectric constant on the frequency, signal level, and direct current (dc) bias field was measured from -55° to 140°C. The dielectric constant (ϵ) below 125°C was considerably dependent on the frequency, the signal level, and dc bias field while ϵ above 125°C was independent. It was concluded that the shell phase was a relaxor. The characteristics of the shell phase were discussed on the basis of the compositional fluctuation in the shell phase and the electrical responses of the dielectric constant.

Key words: BT, Ni-MLCC, core-shell structure

1. INTRODUCTION

Dielectric ceramics based on BaTiO₃ (BT) have been extensively studied since BT is a promising substance especially for multi-layer ceramic capacitors (MLCCs). It is well known that the dielectrics with flat temperature characteristics (TC) of the dielectric constant (ϵ) can be characterized by small grains and so-called "core-shell" structure.¹⁻³ The stability of the core-shell structure is dependent on the composition⁴, the powder handling process⁵, and the firing temperature⁶. Today, the active layer thickness of MLCCs with Ni internal electrode (Ni-MLCCs) under mass production is decreased to below 2 μ m. Adequate controlling and designing of core-shell structures are necessary for obtaining MLCCs for such a high electric field to meet the continuing demand for large capacitance. This is because grains are composed of the core-shell structure in the material having flat TC of ϵ and because the microstructure determines the electrical properties and reliability^{7,8}. Therefore, the objectives of this work are to measure the chemical composition in a grain with the core-shell structure and to better understand the electrical properties of core and shell phase, respectively.

2. EXPERIMENTAL

2.1 Sample Preparation

The main starting material was BT with a nominal average particle size of about 0.35 μ m synthesized hydrothermally (Sakai Chemical Industry Co., Ltd.). Reagent grade MgO, MnO, Ho₂O₃, and BaSiO₃ were weighed and mixed with BT in composition given in Table I and then dried. These powders with an organic binder system were cast into green sheets. A Ni internal electrode was printed on green sheets of about 5 μ m thickness. Twenty-one green sheets with Ni internal

electrodes as well as the protective sheets on the upper and lower sides were stacked and pressed into a bar of about 800 μ m thickness and then cut into small pieces. Terminal Ni electrodes were formed on both sides of the chips. The chips were fired at various temperatures for 2 h, and cooled to 1000°C in a reducing atmosphere controlled by H₂, N₂, O₂, and H₂O, and then to room temperature in a slightly oxidizing atmosphere (P_{O₂}=20 Pa at 1000°C).

Table I. Sample composition (atom%)

BT	MgO	HoO _{3/2}	MnO	BaSiO ₃
100	0.5	1.5	0.1	1.5

2.2 Microstructure Analysis

The microstructure was observed by the field emission scanning electron microscope (FE-SEM; Hitachi, Japan). The diameter of more than 300 grains at the chip surface was measured with a micrometer. The mean grain size was defined as the median value, assuming that each grain was a sphere. A high-resolution analytical electron microscope with an ultrathin-window energy dispersive X-ray detector (HR-AEM; TOPCON 002B, Akashi Co., Ltd., Japan) was used for determining chemical compositions in a grain. The samples were prepared by grinding and ion-milling. The sample and the milling stage were cooled with liquid nitrogen to avoid the creation of artifacts during ion-milling treatment. The phase transition of the samples was characterized by the differential scanning calorimetry (DSC; Macscience, Japan).

2.3 Electrical Properties

TC of the dielectric constant was measured using an LCR meter (HP-4284A; YHP, Japan), covering the

temperature range from -55° to 140°C . The dielectric constant of the chips was calculated geometrically from the thickness and the crossing area of the active layers.

3. RESULTS and DISCUSSION

The volume of the shell phase increases as the firing temperature increases since the shell phase is produced by the reaction with BT and additives.^{3,6} Figure 1 shows the temperature dependence of ϵ for the sample fired at various temperatures. It was found that ϵ increased, particularly below 125°C , and the broad peak around 40°C shifted to higher temperature as the firing temperature increased.

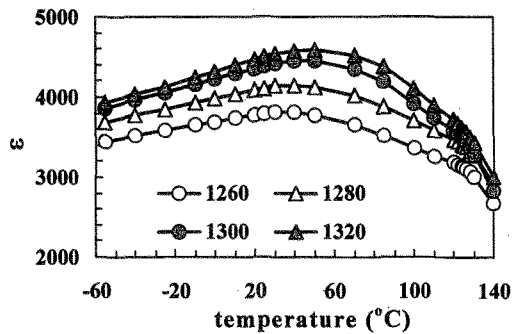


Fig.1 TC of ϵ for the samples fired at various temperatures.

These findings corresponded with the microstructural evolution. Figure 2 shows the mean grain size as a function of the firing temperature. The mean grain size increased gradually as the firing temperature increased.

In addition, Fig.3 shows the DSC profiles of samples fired at various temperatures. All samples showed a

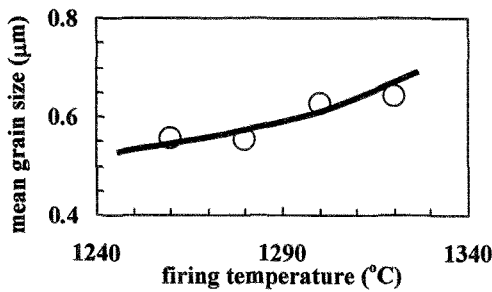


Fig.2 Mean grain size as a function of the firing temperature.

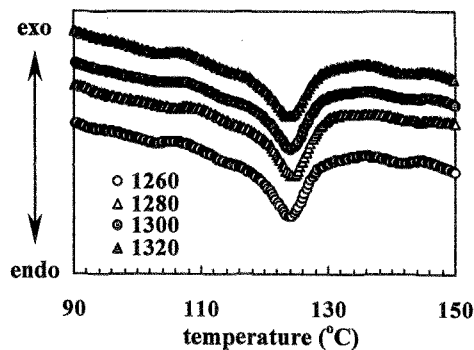


Fig.3 DSC profiles for the sample fired at various temperatures.

broad endothermic peak at around 125°C . A ferroelectric phase transition of the core phase composed of pure BT is responsible for the DSC peak observed at around 125°C .^{3,6} However, no peaks were observed below 125°C in Fig.3 although there was a broad peak at around $40-60^{\circ}\text{C}$ in Fig.1. The gradual increase in the mean grain size seen in Fig.2 and the broadening of the DSC profile at around 125°C seen in Fig.3 can be responsible for the increase in ϵ and the shift of peak seen in Fig.1.

It is important to understand the characteristics of the shell phase. Therefore, the microstructure for the sample fired at 1300°C was observed by HR-AEM. Careful observation for 200 grains revealed that grains of more than 87% were composed of the core-shell structure with a developed shell phase. The typical core-shell structure with a developed shell phase is shown in Fig.4. The composition in a grain was analyzed at several points for two grains as indicated alphabetically in Fig.4. All elements were analyzed in this study. However, only the concentration of Ho, Ba and Ti was reliable, unfortunately. Lack of reliability for Mg, Mn, and Si was due to the small concentration and/or to a contamination in an ion-milling process. The count ratio, Ho/Ti, is listed in Table II. The alphabet in Table II corresponds to that shown in Fig.4. Several facts became clear from Table II. First, Ho did not exist in the center of core region. Secondly, the Ho concentration was rich

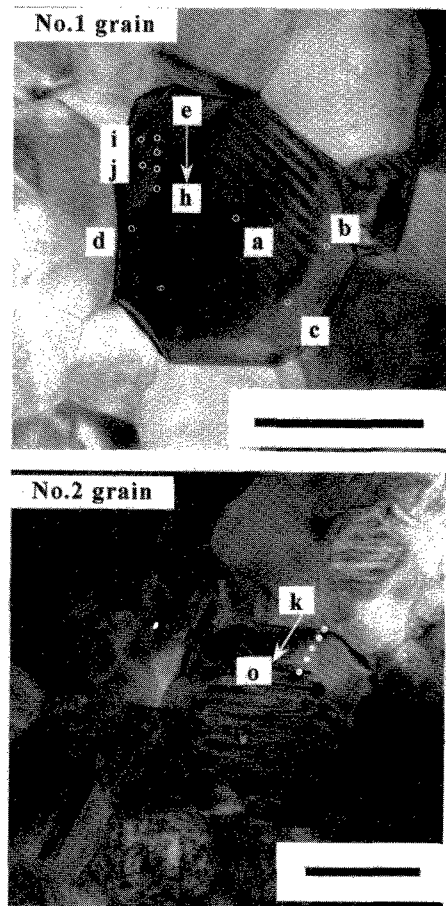


Fig.4 Typical two grains showing the typical core-shell structure and analyzed points by AEM (bar= $0.5\mu\text{m}$).

in grain boundaries. Lastly, the Ho concentration was not constant in the shell phase. The core was not always located at the center of the grain and the thickness of the shell was not uniform. The thin foil for HR-AEM observation must be thick enough to observe domain pattern ($>0.1 \mu\text{m}$) but thin enough to transmit the electron beam ($<0.2 \mu\text{m}$). It is possible that the shell region exists directly under points of h for No.1 grain and o for No.2 grain. Therefore, there is a limit of this compositional analysis in nano-region. However, it was concluded that the core region apart from the core-shell interface did not contain Ho and that there was a concentration fluctuation of Ho in the shell region. The former finding is consistent with the previous papers.^{2,3,9}

Table II Compositional analysis by HR-AEM

		Ho/Ti*	Position
No.1 grain	a	0	Center of core
	b	0.09	shell
	c	0.09	
	d	0.06	
	e	0.07	
	f	0	
	g	0.09	
	h	0.06	
	i	0.08	shell
	j	0.08	
No.2 grain	k	0.12	Grain boundary
	l	0.06	shell
	m	0.06	
	n	0.03	
	o	0	core-shell interface

*count ratio

Rawal *et al.* reported that TC curve of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -doped BT having the core-shell structure showed a broad peak at room temperature, attributed to the shell phase, and another peak near the Curie temperature of BT, attributed to the core phase.⁹ The scattered distribution of Ho concentration implies that the composition fluctuates in the shell phase as pointed out by Pathmarak *et al.*¹⁰ The broad peak at 40-60°C in Fig.1 is ascribed to the shell phase containing fluctuated Ho concentration.

Temperature dependence of TC of ϵ on the frequency, signal level, and dc bias field was, therefore, measured to elucidate the characterization of the shell phase as seen in Fig.5. It was found that ϵ below 125°C increased as the measuring frequency decreased and the signal level increased as seen in Fig.5-a), b) and d). However, ϵ above 125°C was independent on the frequency and signal level. Chazono *et al.* reported a similar signal level response of ϵ in $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ (BTZ) based system ($x=0.14$).¹¹ The increase in ϵ in BTZ based system by applying high signal level was explained as the enhancement of the oscillation of the frozen micro-dipole concerning to the diffuse phase transition.¹² On the other hand, ϵ was dependent on the dc bias field in the whole temperature range measured. Moreover, the broad peak at 40-60°C shifted to lower temperature as the applying dc bias field increased. In BTZ system ($x=0.14$), however, it is well known that the peak of TC of ϵ shifts to higher temperature as the applying dc bias field increases.¹³ The shift to lower temperature of the

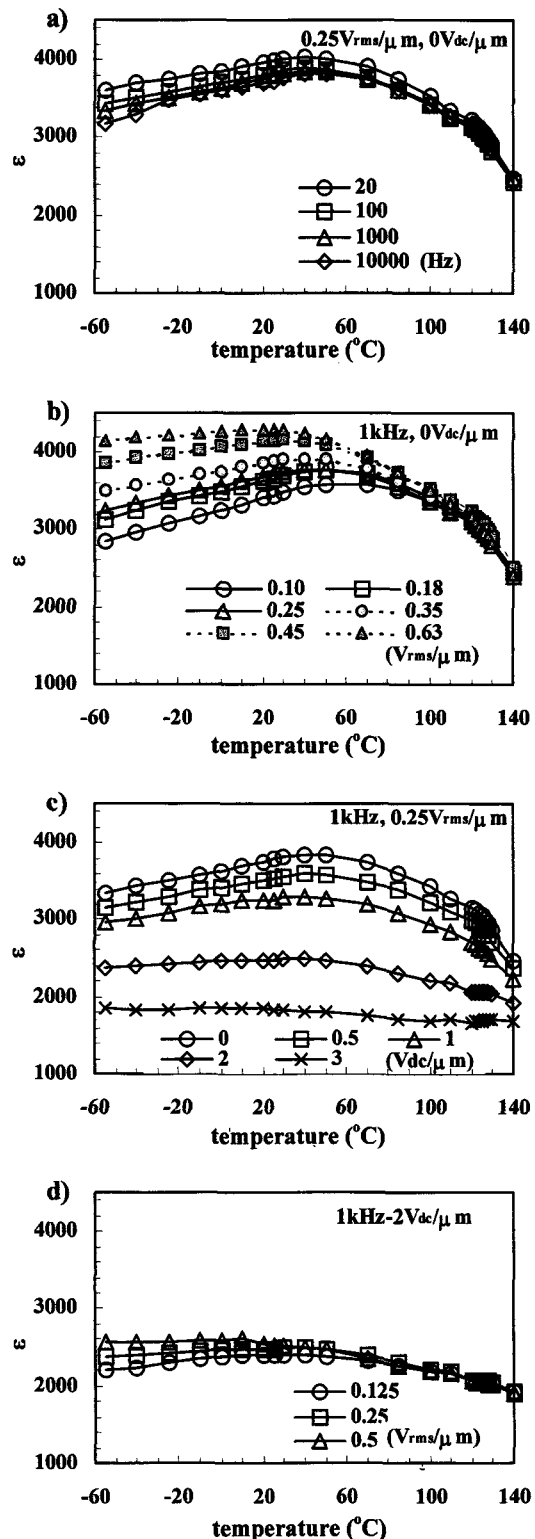


Fig.5 Temperature dependence of ϵ under a parameter of: a) frequency at $0.25V_{rms}/\mu\text{m}$ and $0V_{dc}/\mu\text{m}$; b) signal level at 1kHz and $0V_{dc}/\mu\text{m}$; c) dc bias field at 1kHz and $0.25V_{rms}/\mu\text{m}$; d) signal level at 1kHz and $2V_{dc}/\mu\text{m}$.

TC peak seen in Fig.5-c) is, therefore, caused by some other reason compared with BTZ system. Kighelman *et al.* reported that ϵ decreased and the TC peak of ϵ shifted

to lower temperature in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) thin film when the dc bias field increased.¹⁴ The same phenomena was reported in heavily Zr-rich BTZ system ($x=0.42$), which was explained by the decreased depth of potential well against the polarization.¹⁵ Both material, PMN and heavily Zr-rich BTZ ($x=0.42$), are relaxors. Accordingly, it is concluded that the shell phase is a relaxor due to the similarity to the electrical behaviors of PMN and BTZ ($x=0.42$) as well as the frequency dependence of ϵ below 125°C. These electrical properties must be caused by the compositional fluctuation in the shell phase.

The shell phase is produced by the reaction of the additives with BT and the shell volume is increased as the firing temperature increases.^{3,4,6} The shift of broad peak at around 40°C to higher temperature seen in Fig.1 can be explained by the change of the concentration of additives and their distributions in the shell phase as illustrated in Fig.6. The concentration and its distribution of additives in the shell phase are low and widespread, respectively, when the firing temperature is low as in the case of 1260°C in Fig.1. When the firing temperature is elevated, the concentration of the additives in the shell phase is decreased due to the increase in shell volume. Therefore, the TC peaks contributed by the fluctuated micro-regions in the shell phase will be shifted to higher temperatures. This shift can cause the shift of the broad peak at around 40°C to higher temperature as shown in Fig.1.

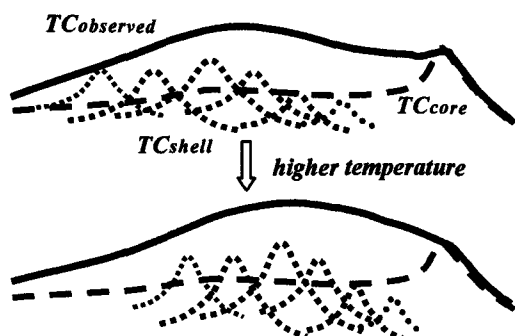


Fig.6 Schematically illustrated TC change of ϵ indicating the compositional change in the shell phase.

4. CONCLUSION

The microstructure and the electrical properties of Ni-MLCC were investigated in BT-MgO-Ho₂O₃ system. SEM observation of Ni-MLCC samples fired at various temperatures revealed that the mean grain size increased gradually as the firing temperature increased accompanied by the decrease and broadening of DSC profile at around 125°C. Ho did not exist in the center of the core region but rich in the grain boundary, judging from HR-AEM analysis. Moreover, Ho concentration fluctuated in the shell phase. It was concluded that the shell phase is a relaxor due to the similarity to the electrical behaviors of PMN and BTZ ($x=0.42$) as well as the frequency dependence of ϵ below 125°C. The compositional fluctuation in the shell phase can be the cause of the electrical properties. The shift of the TC

peak at around 40°C was well explained assuming the change of the concentration of additives and their distributions.

References

- [1] M. Kahn, *J. Am. Ceram. Soc.*, **54** [9] 455-57 (1971).
- [2] D. Hennings and G. Rosenstein, *J. Am. Ceram. Soc.*, **67** [4] 249-54 (1984).
- [3] H. Chazono and H. Kishi, *J. Am. Ceram. Soc.*, **83** [1] 101-106 (2000).
- [4] H. Chazono and H. Kishi, *J. Am. Ceram. Soc.*, **82** [10] 2689-97 (1999).
- [5] Y. Mizuno, Y. Okino, N. Kohzu, H. Chazono, and H. Kishi, *Jpn. J. Appl. Phys.*, **37** [Part I] 5227-31 (1998).
- [6] H. Chazono, Y. Okino, N. Kohzu, and H. Kishi, *Ceramic Transactions*, Vol.97 Ed. by J. -H. Jean, T. K. Gupta, K. M. Nair, and K. Niwa, The American Ceramic Society (1999) pp. 53-64.
- [7] H. Chazono and H. Kishi, "Electroceramics in Japan IV," CSJ Series - Publications of the Ceramic Society of Japan, Ed. By M. Murata, T. Kimura, S. Fujitsu, and K. Shinozaki, Trans Tech Publication Ltd., Switzerland (2000) pp. 47-50.
- [8] H. Chazono and H. Kishi, *Jpn. J. Appl. Phys.*, **40** [Part I] 5624-29 (2001).
- [9] B. S. Rawal, M. Kahn, and W. R. Buessem, *Advances in Ceramics*, Vol.1, Grain Boundary Phenomena in Electronic Ceramics, Ed. by American Ceramic Society, (1981) pp. 172-88.
- [10] S. Pathmarak, M. Al-Khafaji, and W. E. Lee, *Br. Ceram. Trans.*, **93** [3] 114-18 (1994).
- [11] H. Chazono, Y. Inomata, N. Kohzu, and H. Kishi, "Electroceramics in Japan II," CSJ Series - Publications of the Ceramic Society of Japan, Ed. By N. Mizutani, K. Shinozaki, N. Kamehara, and T. Kimura, Trans Tech Publication Ltd., Switzerland (1999) pp.31-34.
- [12] T. Tsurumi, Y. Yamamoto, H. Kakemoto, S. Wada, H. Chazono, and H. Kishi, *J. Mater. Res.*, in press (2002).
- [13] H. Chazono, Y. Inomata, N. Kohzu, and H. Kishi, "Electroceramics in Japan III," CSJ Series - Publications of the Ceramic Society of Japan, Ed. by M. Murata, K. Shinozaki, T. Kimura, Trans Tech Publication Ltd., Switzerland (2000) pp.11-14.
- [14] Z. Kighelman, D. Damjanovic, A. Seifert, S. Hiboux, L. Sagalowicz, and N. Setter, *Integ. Ferro.*, **25**, 125-33 (1999)
- [15] S. Wada, H. Adachi, H. Kakemoto, H. Chazono, Y. Mizuno, H. Kishi, and T. Tsurumi, *J. Mater. Res.*, in press (2002).

(Received December 21, 2001; Accepted January 31, 2002)