Measurement of mechanical properties of BaTiO$_3$ layer in multilayered ceramic capacitor using a microcantilever beam specimen

Hiroshi YAMAGUCHI$^1$, Junichi TATAMI$^{1,7}$ and Motoyuki IIJIMA$^1$

$^1$Yokohama National University, Yokohama 240–8501, Japan

The measurement of the mechanical properties of electroceramics is important for improving the reliability of ceramic components and devices. Although information of the mechanical properties at the microscale level, especially under tensile or bending stress, is desired, this has not yet been reported. In this study, a bending test using a microcantilever beam specimen was applied to measure the mechanical properties of the BaTiO$_3$ layer in a multi-layered ceramic capacitor. As a result, a nonlinearity relationship between stress and strain was observed during the bending test. The bending strength and failure strain, measured using the microcantilever beam specimen, were much higher than those measured using bulk specimens and almost the same or higher than those of conventional Si$_3$N$_4$ ceramics, as the fracture origin was nano-size.

©2019 The Ceramic Society of Japan. All rights reserved.

Key-words : Microcantilever beam specimen, MLCC, BaTiO$_3$ layer, Strength, Young’s modulus, Bending test

1. Introduction

Ceramic components and devices are widely used for functional applications for their excellent electrical properties. The sizes of components and devices get smaller every year. In particular, the dimensions of the components of micro electro mechanical system are at the micrometer level. Furthermore, their structure has become finer to improve their function. For example, the layer thickness of a multi-layered ceramic capacitor (MLCC) is less than 1 μm. In such applications, improvement in mechanical reliability is important, as well as in engineering ceramics, and the mechanical properties must also be evaluated.

Hardness and fracture toughness of functional ceramics was measured by an indentation technique. Furthermore, a bending test is also used to measure the Young’s modulus and bending strength. The ferroelastic behavior of piezo-electric materials is estimated by a compression test. However, in these tests, bulk specimens of millimeter size were used. Therefore, the mechanical properties of the small components or devices with the finer structure indicated above are not measurable.

The nanoindentation technique has been developed to estimate the mechanical properties of small areas. Although this technique is easy and useful, only the hardness and Young’s modulus are measured under a compression stress field. In real applications of electroceramics, the mechanical response under tensile and bending stress fields is more important because ceramics are generally brittle, and there is a possibility that the mechanical properties are different under compressive and tensile stresses.

In recent years, microcantilever beam specimens, machined by the focused ion beam (FIB) technique, are used to estimate mechanical properties, such as bending strength, Young’s modulus, and fracture toughness of materials. For example, the grain boundary fracture toughness of Si$_3$N$_4$ ceramics was directly measured in the bulk specimen. Furthermore, the degradation of the Si$_3$N$_4$ ceramic surface by molten Al was successfully estimated. Although this technique has been useful for pin-point mechanical analysis of materials, only the mechanical properties of structural ceramics have been estimated. In this study, we fabricated a microcantilever beam specimen in the BaTiO$_3$ layer of an MLCC and estimated the mechanical response of the specimen under a bending stress field.

2. Experimental procedures

A commercially available MLCC with a size of 3216 was used in this study. After cutting the MLCC perpendicular to the layers, mirror finishing was performed for the top surface. Figure 1 shows the scanning electron microscope (SEM) images of the polished surface before the preparation of the microcantilever beam specimen. It was clearly observed that the BaTiO$_3$ layer serving as the dielectric and the metal layer as the electrode were alternately laminated [Fig. 1(a)]. The BaTiO$_3$ layer was dense, and it
was composed of fine \( \text{BaTiO}_3 \) grains of less than 1 \( \mu \text{m} \). A microcantilever beam specimen was prepared using the FIB technique (FIB-SEM, JIB-4501, JEOL Ltd., Tokyo, Japan) on the \( \text{BaTiO}_3 \) layer in the polished mirror surface.

The microcantilever beam specimen was prepared using an acceleration voltage of 30 kV and doses of 30, 20, 4.0, and 0.1 ions/cm\(^2\). A small dent was made at the point of 10 \( \mu \text{m} \) from the end of the microcantilever beam specimen to determine the load point in the bending test. Figure 2 shows the microcantilever beam specimen prepared in the \( \text{BaTiO}_3 \) layer. As shown in Figs. 2(a)–2(c), the width, height, and length of the specimen were 1.5, 3.2, and 11 \( \mu \text{m} \), respectively, while its section profile was pentagonal.

The bending test of the microcantilever beam specimen was carried out using a nanoindenter (TI Premier, Bruker, U.S.A.). At first, a topographic image including the microcantilever beam specimen was taken in the scanning probe microscopy mode, equipped with a nanoindenter at a scan rate of 1 Hz. After finding the dent machined on the surface of the specimen as a loading point, the load was applied to the specimen using a cube corner-type diamond indenter (axis-to-plane angle 35.26°). The loading rate was 30 nm/s. The atmosphere in the bending test was air. In the bending test, the relationship between the applied load and displacement at the loading point was obtained, and the fracture load was determined.

According to beam theory in material mechanics, the maximum tensile stress acting on a cantilever beam, like the microcantilever beam specimen used in this study, the strain at this point, and Young’s modulus are calculated by the following equations:

\[
\sigma = \frac{PLa}{I} \quad (1)
\]

\[
\varepsilon = \frac{3da}{L^2} \quad (2)
\]

\[
E = \frac{\sigma}{\varepsilon} = \frac{\Delta PL^3}{3\Delta dI} \quad (3)
\]

where \( \sigma \) is the maximum tensile stress caused by bending, \( a \) is the distance from a neutral surface to the top surface of the specimen, \( \varepsilon \) is the strain at the point of the maximum tensile stress, \( E \) is Young’s modulus, \( P \) is the applied load, \( L \) is the distance from the end of the specimen to the load point, \( d \) is the displacement of the loading point, and \( I \) is the area moment of inertia. The distance from the neutral plane to the specimen surface and the secondary moment of area were estimated using the geometry of the section view of the specimen, as shown in Fig. 2(b). The fracture surface of the microcantilever beam specimen after the bending test was observed by FE-SEM (JSM-7001F, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

Figure 3 shows the load displacement curve of the bending test of the microcantilever beam specimen, prepared in the \( \text{BaTiO}_3 \) layer of the MLCC. The load
initially increased nonlinearly with increasing displacement at the loading point, followed by a roughly linear increase after 400 nm of deformation, in other words, the load-displacement curve was slightly nonlinear. Then, the specimen brittlely fractured when the displacement at the loading point was 1100 nm. The beam theory needs a small deformation. Since the deformation when the microcantilever beam specimen was fractured was smaller than the height and length of the microcantilever beam specimen used in this study, the stress and strain of the microcantilever beam specimen were calculated by applying the beam theory.

Figure 4 shows the stress–strain curve obtained from the load-displacement curve of the microcantilever beam specimen, prepared in the BaTiO$_3$ layer of the MLCC. As reference, the stress–strain curve obtained from the load-displacement curve of Si$_3$N$_4$ ceramics used in the previous study$^{17)}$ is also shown in Fig. 4. The stress of the Si$_3$N$_4$ ceramics increased linearly as the strain increased during loading, and then, brittle fracture occurred. Table 1 indicates the mechanical properties of the BaTiO$_3$ layer in MLCC and the Si$_3$N$_4$ ceramics measured using microcantilever beam specimens. Young’s modulus calculated from the slope of stress–strain curves was 343 GPa for Si$_3$N$_4$ ceramics. Since it was almost the same as that of the dense Si$_3$N$_4$ ceramics measured in the bulk specimens,$^{19)}$ this bending test using the microcantilever beam specimen was judged to be valid. On the other hand, a nonlinear stress–strain curve was found in the bending test using the microcantilever beam specimen of the BaTiO$_3$ layer, exhibited by the load-displacement curve. Young’s moduli calculated from the slope of the initial and medium loads were 62 and 116 GPa, respectively. In general, Young’s modulus of BaTiO$_3$ ceramics has been reported to be in the range of 60 to 170 GPa, depending on porosity and additives.$^{9),14),15),20),21)}$ Although there is no information about density and composition of the BaTiO$_3$ layer used in this study, Young’s moduli measured using the microcantilever beam specimen are also judged to be valid because their values are in the range reported in the previous study. It has also been reported that tetragonal BaTiO$_3$ exhibits ferroelasticity, accompanying the movement of domain walls.$^{13)}$ The nonlinear relationship between the stress and strain in the microcantilever beam specimen prepared from the BaTiO$_3$ layer is expected to result from the domain switching because of high tensile stress and strain without fracture. Linear elastic deformation in the high stress and strain probably occurred because the domain switching was completed.

The bending strength of the BaTiO$_3$ layer, calculated from the maximum load, was 4.1 GPa, which was much higher than that measured using the millimeter-sized specimen.$^{10),12)}$ This value is almost as high as the bending strength estimated using the microcantilever beam specimens of Si$_3$N$_4$ ceramics, which are typical engineering ceramics. In brittle materials, the higher strength in the smaller specimen is known as the size effect of the strength, resulting from the decrease in the defect size. Figure 5 shows the fracture surface of the microcantilever beam specimen. It was observed that the fracture occurred at the end of the microcantilever beam specimen [Fig. 5(a)]. This means that the maximum stress estimated from the fracture load and the sample geometry should be the bending strength of the microcantilever beam specimen. As shown in Fig. 5(b), the fracture mode of the BaTiO$_3$ layer was transgranular and intergranular. Furthermore, a small pore of about 50 to 100 nm, indicated by the arrow in Fig. 5(b), existed near the tensile surface. The equivalent crack size, $2c$, estimated from the Griffith equation using the measured bending strength in this study and the fracture toughness of the BaTiO$_3$ ceramics reported in the previous study (1.14 MPa m$^{1/2}$),$^8$ was about 50 nm. This was in agreement with the size of the pore observed on the fracture surface. From this fractography, the pore seems to be of a fracture origin, though a typical mirror region was not observed. In future work, the fracture origin will be clarified by the development of novel fractography techniques. The failure strain of the BaTiO$_3$ layer in the MLCC was about 4%, which was about 2.5 times as high as that of the Si$_3$N$_4$ ceramics. This large failure strain has not been found in the bulk specimens, and it is peculiar to mechanical properties at the microscale level. Consequently, it was shown that the bending test using microcantilever beam specimens is an effective and useful tool to estimate mechanical properties at the microscale level.

Table 1. Mechanical properties of the BaTiO$_3$ layer in MLCC and the Si$_3$N$_4$ ceramics measured using microcantilever beam specimens

| Mechanical property | BaTiO$_3$ layer | Si$_3$N$_4$ ceramics |
|---------------------|----------------|---------------------|
| Young’s modulus/GPa | 62$^{20)}$      | 343                 |
| Bending strength/GPa| 116$^{b)}$      | 5.89                |
| Failure strain/%   | 4.1            | 1.6                 |
| Equivalent crack length 2c/nm | 50           | 99                  |

a) calculated from displacement between 100–200 nm.  
b) calculated from displacement between 800–1000 nm.
4. Conclusions

The mechanical properties of the BaTiO₃ layer in MLCC were successfully measured using the microcantilever beam specimen. The stress–strain curve of the BaTiO₃ layer was determined to be nonlinear through the bending test. The bending strength and failure strain, measured using the microcantilever beam specimen, were much higher than those measured using millimeter-size specimens. It was confirmed that the bending test using the microcantilever beam specimen is a useful tool to evaluate the mechanical properties at the microscale level, as specific properties resulting from very high tensile stress appear.

Acknowledgements This work was partly supported by JSPS KAKENHI Grant Numbers 17H01319.

References
1) K. Kaneda, Y. Iwazuki and Y. Konishi, J. Ceram. Soc. Jpn., 126, 931–935 (2018).
2) S. M. Halle, Acta. Mater., 51, 5981–6000 (2003).
3) Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Nature, 432, 84–87 (2004).
4) C. Matsunaga, Y. Zhou, D. Kusano, H. Hyuga and K. Hirao, J. Ceram. Soc. Jpn., 126, 693–698 (2018).
5) Y. Imanaka, H. Sano, M. Osada, T. Tsuchiya, K. Kakimoto and H. Moriwake, Bull. Ceram. Soc. Jpn., 51, 830–835 (2016) [in Japanese].
6) W. M. Zhang, H. Yan, Z. K. Peng and G. Meng, Sensor. Actuat. A-Phys., 214, 187–218 (2014).
7) Y. I. Shin, K. M. Kang, Y. G. Jung, J. G. Yeo, S. G. Lee and U. Paik, J. Eur. Ceram. Soc., 23, 1427–1434 (2003).
8) G. A. Schneider and V. Heyer, J. Eur. Ceram. Soc., 19, 1299–1306 (1999).
9) F. Cordero, J. Appl. Phys., 123, 094103 (2018).
10) S. Seo and A. Kishimoto, J. Eur. Ceram. Soc., 20, 2427–2431 (2000).
11) S. Sakamoto and Y. Sugimoto, Bull. Ceram. Soc. Jpn., 432, 84–87 (2004).
12) M. R. Tohidifar, Acta. Mater., 55, 6472–6480 (2007).
13) S. S. Ryu, H. T. Kim, H. J. Kim and S. Kim, J. Ceram. Soc. Jpn., 117, 811–814 (2009).
14) A. Rar, G. M. Pharr, W. C. Oliver, E. Karapetian and S. V. Kalinin, J. Mater. Res., 21, 552–556 (2006).
15) J. Tatami, M. Katayaam, M. Ohnishi, T. Yahagi, T. Takahashi, T. Horiuchi, M. Yokouchi, K. Yasuda and D. K. Kim, J. Am. Ceram. Soc., 98, 965–971 (2015).
16) S. Fujita, J. Tatami, T. Yahagi, T. Takahashi and M. Iijima, J. Eur. Ceram. Soc., 37, 4351–4356 (2017).
17) A. D. Norton, S. Falco, N. Young, J. Severs and R. I. Todd, J. Eur. Ceram. Soc., 35, 4521–4533 (2015).
18) T. Rouxel, J. Ceram. Soc. Jpn., 109, 589–598 (2001).
19) T. Trzepiecinski and M. Gromada, Mater. Sci.-Pol., 36, 151–156 (2018).
20) S. Jiansirisomboon and A. Watcharapasorn, Curr. Appl. Phys., 8, 48–52 (2008).