Characterization of mechanical properties of BaTiO$_3$ ceramic with different types of sintering aid by nanoindentation

Sung-Soo RYU,† Hyung-Tae KIM, Hyeong Jun KIM and Seongwon KIM

Engineering Ceramic Center, Korea Institute of Ceramic Engineering & Technology, Gyeonggi-do 467-843, Korea

The influence of glass composition on mechanical property of BaTiO$_3$ ceramics was investigated with nanoindentation technique and also its effect on densification and dielectric property was analyzed. Two different glasses of BaO–CaO–SiO$_2$ and BaO–ZrO$_2$–SiO$_2$ system were used as the sintering aid of BaTiO$_3$ powder. It was found that the addition of BaO–ZrO$_2$–SiO$_2$ glass to BaTiO$_3$ was beneficial for the densification compared to that of BaO–CaO–SiO$_2$ glass, resulting in high dielectric constant over 2500, the hardness value of 13.6 GPa and the elastic modulus of 167.9 GPa after sintering at 1240°C.

Key-words : BaTiO$_3$, Glass, Nanoindentation, Mechanical property, MLCC

1. Introduction

Barium titanate (BaTiO$_3$) ceramic, which is one of the most widely used materials in electric ceramics, has been utilized in primary materials for multi layer ceramic capacitor (MLCC), electro-optic devices and thermostor because of its highly dielectric characteristics.\(^1\)

As the need for MLCC of high capacitance with small size increases, the number of dielectric ceramic layers increases and the thickness of the ceramic layers decreases.\(^2\) This could cause mechanical failure due to the difference in density between electrode and margin layer without electrode.\(^3\) And also the development of residual stresses within the BaTiO$_3$ ceramic layers becomes more pronounced and knowledge concerning them becomes more important, not only from the viewpoint of mechanical stability and lifetime, but also from the viewpoint of improved performance, i.e., higher dielectric constant.\(^3\)

The estimation for the mechanical property of BaTiO$_3$ for understanding of an internal stresses induced on MLCCs is essential for improving the reliability and the lifetime of MLCCs. Several researchers have performed the measurement of the internal stresses (residual stresses) by the sharp indentation method using a micro-indentor such as Vickers test.\(^3\),\(^4\)

However, generally, Vickers tests at an applied load of 10–500 g result in indentations with diagonals ranging from 10 to 100 $\mu$m and depths from 1 to 10 $\mu$m.\(^5\) Thus, in the case of high capacitance MLCC with very thin BaTiO$_3$ dielectric layer below 2 $\mu$m, these applied loads are comparatively too large to measure its mechanical property within the dielectric thin layer. Since nanoindentation technique can, unlike the Vickers method, measure mechanical properties in very small areas under very low loads,\(^6\)–\(^9\) it is an important tool in understanding mechanical property in thin film, composite materials and layered materials.\(^10\)–\(^12\)

However, to author’s knowledge, there are few researches on the measurement of mechanical property for BaTiO$_3$ sintered ceramic itself by a nanoindentation method. Thus, in this study, the nanoindentation method was used for the measurement of the mechanical properties of BaTiO$_3$ sintered ceramic. On the other hand, the glass composition, which acts as a fluxing agent for liquid phase sintering as well as a modifier of the dielectric property of BaTiO$_3$, may be very important parameter in controlling the mechanical property of BaTiO$_3$ by lowering sintering temperature of BaTiO$_3$ ceramic, increasing its densification and making its grain size fine.\(^13\),\(^14\) Thus, two different glasses of BaO–CaO–SiO$_2$ and BaO–ZrO$_2$–SiO$_2$ were used as the sintering aid for the densification of BaTiO$_3$ ceramic in this study. The influence of types of the glass composition on mechanical property of BaTiO$_3$ was investigated by nanoindentation test and also their effect on the densification behavior and the dielectric property was studied.

2. Experimental procedure

Commercial BaTiO$_3$ powder (Hydrothermally synthesized, Sakai Chemical Industry Co., Ltd., BT–03) with a particle size of 300 nm was used throughout this study. The additives included 1.4 mol% MgCO$_3$ (Kojundo Chemical Co., Ltd.), 0.15 mol% MnO$_2$ (Kojundo Chemical Co., Ltd.), 0.6 mol% Y$_2$O$_3$ (Kojundo Chemical Co., Ltd.) and 1.5 mol% sintering aid.

Two BaO–CaO–SiO$_2$ (BCS) and BaO–ZrO$_2$–SiO$_2$ (BZS) glass systems were chosen for a sintering aid of BaTiO$_3$ powder in this study. These two types of glass composition, BaO–22 wt%CaO–5 wt%SiO$_2$ and BaO–15 wt%ZrO$_2$–70 wt%SiO$_2$, were prepared by mixing the raw BaO, CaO, ZrO$_2$ and SiO$_2$ as starting materials and melting them in a platinum crucible in an air atmosphere at 1300°C for 2 h. The molten glasses were quenched on a platinum plate cooled by water and were milled with zirconia ball of 3 mm diameter for 24 h in a Planetary mill. Glass powders had irregular shape and the specific surface areas were 4.1 m$^2$/g for BCS glass and 8.7 m$^2$/g for BZS glass.

The weighed sintering BaTiO$_3$ powder, all the doping oxides and glass powder were first mixed by ball milling with zirconia media of 3 mm diameter for 20 h. Formulated BaTiO$_3$ powders were mixed with an organic binder, ethyl alcohol and toluene to prepare slurries. Ceramic green films were prepared using the doctor blade method, then stacked, pressed and cut to a rectangular shape with the size of 10 mm width, 10 mm length and 5 mm thickness. The burnout process to remove the organic binders was performed 300°C for 3 h and the sintering process was...
carried out in H₂–H₂O–N₂ atmosphere (P O₂ ~10⁻¹¹ atm) with a wet atmosphere (20°C, H₂O) between 1220°C and 1260°C for 2 h. The heating rate was at constant rates of 5°C/min.

Bulk density of sintered specimen was measured using Archimedes method to check its densification. The capacitance and dissipation factor were measured at 1 kHz and 1.0 Vrms, using a LCR meter (HP–4284A).

Before the nanoindentation test was made, the sintered BaTiO₃ specimens were carefully polished to minimize surface roughness. Hence, the possible effects of rough surfaces (on hardness and modulus measurements) were minimized. The measurements of hardness and modulus were performed using a TriboScope (Hysitron Inc., Minneapolis, MN) Nanomechanical Testing System integrated with a DI Dimension 3100 AFM frame. A three-plate capacitive transducer was used by the TriboScope system to control the applied load and displacement. Within the system, the standard cantilevered AFM tip was replaced with a diamond indenter. This served as both the indenter probe and an imaging probe, thereby eliminating any uncertainty in locating the indentation after unloading. A Berkovich (three-sided pyramid tip, 142.3°) diamond indenter was used in this study. The loading profiles included three segments: loading to a peak load; holding at the peak load; unloading back to the zero load. Loading and unloading rates of 1.0 mN/s were applied. Load of 5 mN was applied to BaTiO₃ sintered specimen for holding period 2 s. Furthermore, in an effort to decrease the possible interactions between indents, all the indents were separately by 20 μm. The measurements were repeated 10 times for each sample.

3. Results and discussion

Figure 1 shows the densification of hydrothermal BaTiO₃ ceramic sintered with BCS and BZS glasses at various temperatures for 2 h. As shown in this figure, the sintered density of BaTiO₃ with BCS glass increased continuously with sintering temperature, while the sintered density of BaTiO₃ specimen with BZS glass increased slightly with sintering temperature up to 1240°C, where maximum density of 5.83 g/cm³ was achieved, and were higher than compared to that of BaTiO₃ added by BCS glass. It indicates that the densification of BaTiO₃ depends on the glass composition and the addition of ZrO₂ to BaSiO₃ glass system is able to lower the sintering temperature for the densification of BaTiO₃.

Figure 2 shows the dielectric constants and dielectric loss at room temperature, measured at 1 kHz, for BaTiO₃ ceramic sintered with various glasses. It occurs that the nature of the glass may influence to the dielectric constant values of sintered BaTiO₃ ceramics. For the BaTiO₃ sintered with BCS glass, the dielectric constant increased abruptly from 2000 to 2450 with sintering temperature, while the sintered BaTiO₃ specimen with BZS glass was characterized by a higher dielectric constant value over 2500 irrespective of sintering temperature, which seemed to be due to the fact that a better densification has been obtained compared to the addition of BCS glass as can be seen Fig. 1. In addition, the increase in dielectric constant could be attributed to diffusion of Zr⁺ into the BaTiO₃ lattice as well as its effect in decreasing the grain size. Armstrong et al. reported that the addition of ZrO₂ to CaO₂B₂O₃ fluxed BaTiO₃ system led to decrease in grain size, resulting in significant increase in the room temperature dielectric constant. Figure 2(b) shows dielectric loss of BaTiO₃ sintered specimen. As shown in this figure, all specimens showed a low degree of dielectric loss below 2.5% which generally satisfied the X7R temperature specification. However, dielectric loss of BaTiO₃ sintered specimens with BZS glass was more stable in entire range of sintering temperature than that of BaTiO₃ sintered with BCS glass.

Figure 3 shows a typical load-displacement curve for BaTiO₃ sintered specimen obtained in the nanoindentation tests. The samples, which were sintered 1240°C for 2 h, were subjected to
nanoindentation to maximum loads of 5 mN and their load–displacement curves revealed a typical remaining plastic deformation. Doerner and Nix,7) and later on Oliver and Pharr,8) and Pharr et al.9) developed a most comprehensive method for determining the hardness and modulus from depth sensing indentation load–displacement data. In the theory, the Meyer’s definition of hardness, $H$, was adopted. This is given by:

$$H = \frac{P_{\text{max}}}{A}$$  \hspace{1cm} (1)

Where, $P_{\text{max}}$ is the maximum load and $A$ is the projected contact area. The tip area, $A$ was first calibrated by indenting on the standard fused quartz sample from Hysitron Inc., which is the maker of nanoindentation equipment. With a constant modulus assumption for quartz sample, $A$ was calculated for each indent. Then, the computed area $A$ was plotted as a function of contact depth $h_c$ and a fitting procedure was employed to fit the $A$ versus $h_c$. Using this approach, $A$ was determined with the help of software program for the Berkovich indenter in the current study. The recorded load-displacement data were used to relate the stiffness, $S$, from the slope of the initial unloading curve, to the reduced elastic modulus, $E_r$:

$$E_r = \frac{\sqrt{2} S}{\sqrt{A}}$$  \hspace{1cm} (2)

Where, $S$ is the contact stiffness corresponding to the slope of the load–penetration curve at the beginning of the unloading. Using the Eqs. (1) and (2), the hardness and elastic modulus was calculated from data in load-displacement curve of Fig. 3. The results showed that the hardness of BaTiO$_3$ specimens with BCS and BZS glasses were 12.0 GPa and 14.1 GPa, respectively and their elastic modulus were 156.5 GPa and 173.6 GPa, respectively. In order to investigate the dependence of glass type on mechanical properties of BaTiO$_3$ ceramic in detail, the nanoindentation measurements for specimens sintered at various sintering temperatures were carried out.

Figure 4 shows the hardness of BaTiO$_3$ specimens sintered at various temperatures for 2 h by nanoindentation measurements. The change of hardness values revealed the similar trend to that of hardness values. BaTiO$_3$ specimen sintered with BZS glass had higher elastic modulus value than BaTiO$_3$ with BCS glass and its value increased from 164.6 GPa at 1220$^\circ$C to the maximum value of 167.9 GPa at 1240$^\circ$C and then slightly decreased to 160.4 GPa at 1260$^\circ$C. For BaTiO$_3$ specimen sintered with BCS glass, the hardness increased continuously with sintering temperature and reached to 12.3 GPa at 1260$^\circ$C. For BaTiO$_3$ specimen sintered with BCS glass, the elastic modulus increased continuously with increasing sintering temperature and reached to 156.0 GPa at 1260$^\circ$C. This tendency of the hardness and the elastic modulus values with types of glass system agrees well with the results of the behavior of densification in Fig. 1. BaTiO$_3$ system was usually densified via liquid phase sintering mechanism by melting of glass composition. Thus, glass composition played an important role in sintering behavior of BaTiO$_3$. In this study, the glass composition affected the sintered density of BaTiO$_3$ and specimen with high sintered
density showed high hardness and elastic modulus. Furthermore, since glass phase did not form a thin layer and randomly distributed in grain boundary of BaTiO$_3$ particles after finishing sintering process, it is difficult to indent individual BaTiO$_3$ and glass phases. Thus, mechanical property on indent in this study seems to be affected by the interaction between BaTiO$_3$ phase and by glass phase. On the other hand, although at sintering temperature of 1260°C both specimens had similar density regardless of glass type, the hardness and the elastic modulus of BaTiO$_3$ specimen with BZS was higher than that of BaTiO$_3$ specimen BCS glass. This means that the addition of ZrO$_2$ to the glass composition has a positive influence on improving mechanical properties of BaTiO$_3$ ceramic.

Figure 6 shows AFM image for typical indents on BaTiO$_3$ sintered specimens with BZS glass after a nanoindentation test. As shown in this figure, the diagonal size of indent was below 2 μm. From this result, it is expected that a nanoindentation technique is applicable for measuring mechanical properties of a MLCC chip with very thin layer below 2 μm.

4. Conclusions

Two different glasses of BaO–CaO–SiO$_2$ and BaO–ZrO$_2$–SiO$_2$ were used as the sintering aid for the densification of BaTiO$_3$ ceramic. The effect of glass composition on the densification of BaTiO$_3$ ceramics using nanoindentation technique was investigated and also its effect on the densification and dielectric properties was analyzed. The addition of BZS glass with BaTiO$_3$ powder led to higher densification compared to the specimen with BCS glass and was helpful to reduce the sintering temperature. The dielectric constant increased from 2000 to 2450 with sintering temperature for the BaTiO$_3$ sintered with BCS glass, while the sintered BaTiO$_3$ specimen with BZS glass was characterized by a higher dielectric constant value over 2500 irrespective of sintering temperature. The results of nanoindentation test showed that the hardness and elastic modulus depended on the densification behavior of BaTiO$_3$ as well as the glass composition. It is concluded that a nanoindentation technique seems to be applicable for measuring mechanical properties within BaTiO$_3$ dielectric layer of very thin thickness in high capacitance MLCC.

References