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Dielectric Properties and Microstructure of Sintered $BaTiO_3$ Using 80 nm Particles with Variation of Additives for MLCCs†

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For the purpose of ultra-thin layer MLCC application, a commercial $BaTiO_3$ dielectric powder with an average particle size of 80 nm was used to apply additives, such as Dy, Mg, Mn, Si, Ba and Ca, by a coating method and the microstructure and dielectric properties of $BaTiO_3$ sintered materials were investigated, as a function of the employed additives. Fixing Mn and Dy ions at 0.2 and 0.75 mol %, respectively and additionally varying Si and Mg from 1 to 1.5 mol % and from 1 to 2 mol %, respectively, the additives were sintered in a reducing atmosphere. Based on the results of an investigation of dielectric properties, Ba 1 mol % and Ca 1 mol % were added and Si and Mg ions were also added to check whether they are applicable to the MLCC composition. With an increase in the amount of Si added, grains were found to grow. In the case of Mg, the grain growth was not controlled even when its amount was increased to 2 mol %. On the other hand, with the addition amount of 2.5 mol %, the grain growth was controlled, consequently resulting in a microstructure having particles with uniform size. The composition with added Ca and Ba, which is known as a depressor, led to large grain growth. Consistent dielectric properties were identified according to changes in grain size and densification and the composition with added Mn (0.2 mol %), Dy (0.75 mol %), Si (1.5 mol %) and Mg (2.5 mol %) met the condition of X6S, temperature dependencies of dielectric constant, having uniform microstructure and reaching a dielectric constant of over 2000 at room temperature.

Keywords: MLCC, 80 nm $BaTiO_3$, Variation of additives, Dielectric thick film.

INTRODUCTION

$BaTiO_3$, a representative ferroelectric ceramic, is widely used as a MLCC material. In recent trends of miniaturization and high functionality electronic equipment, the dielectric layer thickness of MLCC has been ultra-thin. In order to form this ultra-thin dielectric layer, efforts to apply much smaller-sized nano $BaTiO_3$ particles are being made[1-4].

As MLCC must ensure temperature dependencies of the dielectric constant and control grain size influenced by decreased thickness of the dielectric layer, various additives should be used. They are known to form core-shell structures by controlling the inside and boundary of grains in the process of sintering[5-7]. Representative additives include Si ions, the primary material in liquid phase formation for low temperature sintering and Mg ions, which are known to inhibit grain growth[8,9]. Additional additives include Mn, Dy and Y, which are known to contribute to improve properties and reliability of non-reduction. Other additives, such as Ba and Ca, whose phase transition is known to act as a depressor with respect to temperature and consequently contributes to temperature stability, have been reported but it is difficult to strictly classify the role of these additives in the sintering environment[10-14].

Many study results have been reported on the MLCC composition and many companies have already commercialized it and manufactured relevant products. However, it is known that when small particles are formed into small grains, development of domains inside the grains is hampered, thereby dramatically lowering the dielectric constant[2,15]. Therefore, a sufficient dielectric constant should be ensured for application of 80 nm-sized $BaTiO_3$ powder. To this end, a conceptual change is necessary in the existing study on MLCC composition related to compact core-shell structures without particle growth. Furthermore, research on the control of uniform microstructure and properly sized particle growth is necessary. However, there have been few studies on MLCC compositions using 80 nm sized-$BaTiO_3$ particles.

In the present study additives including Mg, Si, Mn and Dy were coated on 80 nm sized-$BaTiO_3$ particles, which can be used on a commercial scale to examine the post-sintering

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dielectric microstructure resulting from changes in Mg and Si composition and to measure dielectric constant resulting from changes in additive composition. Based on these results, Ba and Ca were added and Mg and Si were further added in order to optimize a MLCC composition using 80 nm-grade $BaTiO_3$.

EXPERIMENTAL

The powder used was $BaTiO_3$ with 80 nm particle size (Toda Kyogo, Japan). Regarding the addition method of additives, each composition was coated based on liquid coating of additives, rather than on a mixture of the existing oxide particles, so that a uniform composition could be secured. For additives, metallo-organic compounds that can dissolve in a solvent were reviewed and used and the sources used are described in Table-1.

TABLE-1
GENERAL PROPERTIES OF POWDERS AND ORGANICS

Compounds	Specification
$Mg(C_2H_3O_2)_2{\cdot}4H_2O$	99.9 %, high purity chemicals co. Ltd., Japan
$C_6H_9DyO_6{\cdot}H_2O$	99.9 % Sigma-Aldrich co. LLC., USA
$Mn(CH_3COO)_2{\cdot}4H_2O$	99.9 % high purity chemicals Col. Ltd., Japan
$(CH_3COO)_2Ba$	99.999 %, Sigma-Aldrich Co. LLC., USA
$Ca(CH_3COO)_2{\cdot}xH_2O$	99 % High purity chemicals Co. Ltd., Japan
$Si(OC_2H_5)_4$	99.9999% high purity chemicals Co.Ltd., Japan
Ethanol	99.9 % Daejung chemicals & metals Co. Ltd., Korea
Dispersant	BYK Chemie, Germany
D.I. water	–

The additives were manufactured with an aqueous solution with constant concentration so they could be added in liquid phase. At this time, only the Dy source of $C_6H_9DyO_6{\cdot}xH_2O$ was dissolved in distilled water while other additives sources were dissolved in ethanol. The amount of additives added was determined corresponding with the number of each metallic ion mole calculated against $BaTiO_3$ 1 mol. $Mn(CH_3COO)_2{\cdot}4H_2O$ and $C_6H_9DyO_6{\cdot}xH_2O$ were fixed at 0.2 and 0.75 mol %, respectively. For $Si(OC_2H_5)_4$, the amount added ranged from 1 to 1.5 mol %. The amount of $Mg(C_2H_3O_2)_2{\cdot}4H_2O$ added varied from 1 to 2 mol % at an interval of 0.25 mol %. The microstructure and dielectric properties depending on the amount of Si and Mg added were analyzed and then the composition with addition of Ba 1 mol % and Ca 1 mol % and the composition with further addition of Si and Mg ions were coated to investigate the optimum choice for a MLCC composition.

In order to obtain the powder coating, $BaTiO_3$ particles were dispersed in solution with melted additives before the additives were coated by using a pressure-reducing paste mixer, where mixing and drying could occur simultaneously. According to the designed process, a solvent is volatilized and dried under decompression and even in the course of drying, mechanical mixing continues to extract additives on surface of nanoparticles, resulting in uniform coating. $BaTiO_3$ 30g of 80 nm, a small amount of dispersing agent and zirconia balls of 3Φ and 1Φ were all together put in a 150 cc-large container with addition of solution with uniformly dissolved additive sources according to composition percentage. The mixed base materials were coated at 1600 rpm for 1 h and subsequently used to produce a coated powder with each MLCC composition calculated. The coated powder was heated at 500 ºC for 2 h to decompose organic components included in the additives' metallo-organic compounds.

After granulating with PVA melted in distilled water, 100 MPa pressure was applied to the completely coated powder by using a 10 nm diameter mold, followed by formation with a pallet. The produced sample was subjected to a 5 h-long bake at 500 ºC and sintered at 1200 ºC for 2 h under a reducing atmosphere. Ag paste was printed over the surface of the sintered sample and electrode baking was conducted at 600 ºC.

Bulk density of the sintered body was measured by using Archimedes method and the microstructure was assessed by a scanning electron microscope (JSM 6700F, Jeol, Japan). For dielectric properties of a material, an Impedance Analyzer (HP 4194A) was used to measure the temperature dependence of the dielectric constant with application of cooling and heating temperature from -50 to 155 ºC as well as a normal temperature dielectric constant at 1 kHz.

RESULTS AND DISCUSSION

Fig. 1 displays an electron microscope image of $BaTiO_3$ powder used in this experiment. As seen in the figure, although expected to have significantly high surface energy due to the uniform and small particle size of 80 nm and large specific surface area of 12.85 m^2/g, the powder particles, a base material on a commercial scale, were fully dispersed in the synthesis and dispersion processes and as a result less flocculation was identified in a dry condition.

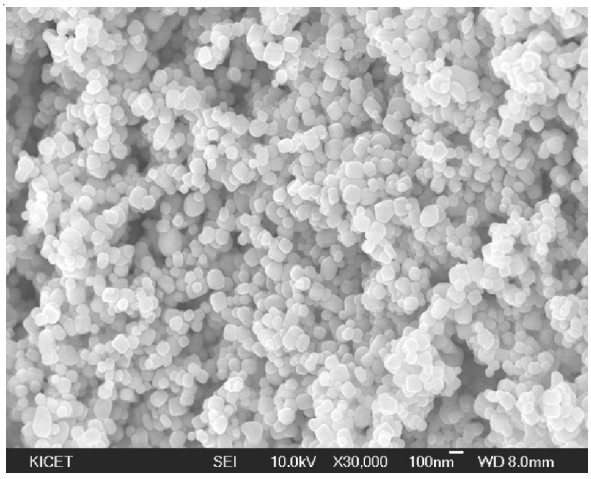

Fig. 1. SEM image of 80 nm $BaTiO_3$ powder

Using this powder, additives were coated based on each composition and sintered under a reducing atmosphere of 1200 ºC before bulk density was measured (Fig. 2). Among the additives, Mn and Dy ions were fixed at 0.2 and 0.75 mol %, respectively. And as a result of measuring the bulk density of the sintered specimen according to changes in the amounts of added Mg and Si, the composition with the addition of 1.5 mol % and less Mg was found to have high density with a greater amount of Si ions (1.5 mol %). On the other hand, the composition with the addition of 1.5 mol % and highe Mg was found to have high density with a smaller amount of Si ion (1.0 mol %).

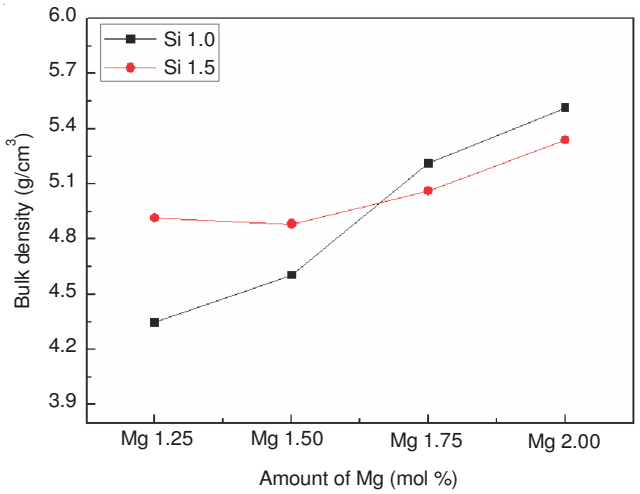

Fig. 2 Bulk density of the sintered bodies at 1200 ºC for 2 h with the amounts of Si and Mg additives (Mn 0.2, Dy 0.75 mol %)

Additionally, it was identified that regardless of the amount of Si added, the bulk density increased with an increasing rise in the amount of Mg. According to a previous report, it is known that Mg remains in the grain boundary, thus causing a delay in necking between BT particles[16]. However, considering that the density increases with a rise in the amount of added Mg ions and interaction takes place in the density change related to Mg ions, as in the case with Si ion, it is concluded that Mg, like Si ion, forms a liquid phase and promotes densification and grain growth. From the perspective of the phase diagram related to $BaTiO_3$ composition, it is known that the liquid can be created with SiO_2 being a primary composition and MgO and BaO being added and TiO_2 and the liquid phase can be properly created at about 1400ºC with a composition including SiO_2 and MgO[17]. In this experiment, where $BaTiO_3$ particles are 80 nm-sized nanoparticles and additives are coated on an atomic unit, the liquid phase is thought to be properly created even at the low sintering temperature of 1200 ºC.

Fig. 3 shows the microstructure of the specimen sintered at 1200 ºC for 2 h based on a composition whose amount of added Mg ions is varied in a range of between 1.2 and 2 mol % with Mn (0.2 mol %), Dy (0.75 mol %) and Si (1.0 mol %) being added. Fig. 3a) is the microstructure with the addition of Mg 1.25 mol %. In the figure, grains have already grown to 200 nm but are not fully densified because the amount of liquid phase required for densification is not sufficient. However, as seen in Figs. 3(b-d), where the amount of added Mg ions increases gradually, the densification process is investigated qualitatively and it is consistent with results of density in Fig. 2. However, the grain growth is not inhibited and, rather, larger grains appear. In particular, grains of 1 μm and over are observed in Fig. 3(d). This is in discord with a report by Kishi *et al.*[8] that Mg acts as an inhibitor of particle growth within the $BaTiO_3$ grid to inhibit grain growth. In other words, the finding that, despite an increase in the amount of added Mg ions, the grains are not prevented from growing and rather grow larger indicates that Mg ions are involved in the liquid phase.

Fig. 4 illustrates the microstructure of the specimen sintered at 1200 ºC for 2 h based on the composition whose amount of added Mg ions was varied in a range of 1.2-2.0 mol %

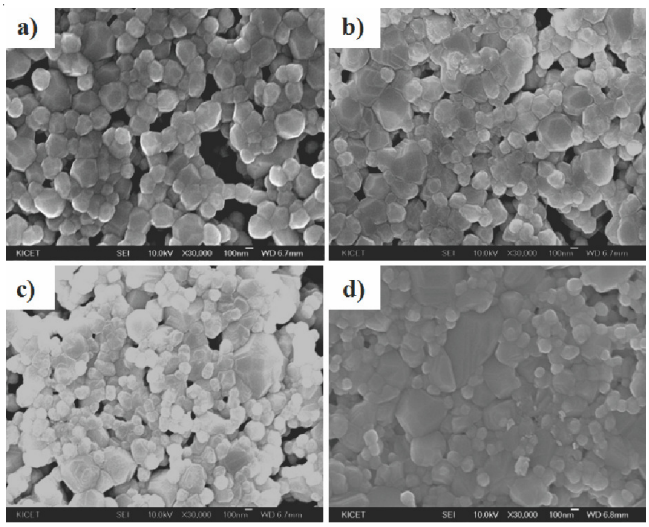

Fig. 3. Microstructures of sintered $BaTiO_3$ at 1200 ºC for 2 h with the amounts of Mg; (a) Mg 1.25 mol %, (b) 1.50 mol %, (c) 1.75 mol % and (d) 2.00 mol % (Si 1.0 Mn 0.2, Dy 0.75 mol %)

with addition of Mn (0.2 mol %), Dy (0.75 mol %) and Si (1.5 mol %) under the condition that the amount of Si, which is a critical factor in controlling the liquid phase amount, is increased. As seen in Fig. 4(a), grain growth is identified with 1 μm-sized grains being observed. A similar trend was found when the amount of added Mg ions was increased. However, under the condition where 2 mol % Mg ions were added, it was found that the grain growth was not inhibited. In contrast with previous reports, it is concluded that when Mg ions are added to 80 nm $BaTiO_3$, they do not sufficiently work as an inhibitor of grain growth[8,18].

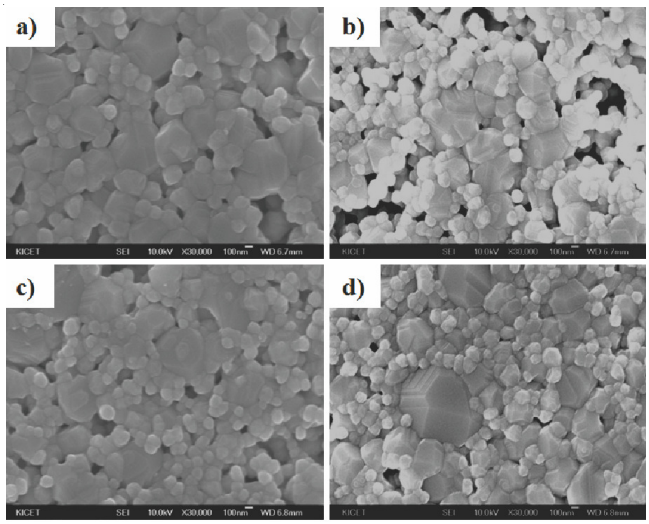

Fig. 4. Microstructures of sintered $BaTiO_3$ at 1200 ºC for 2 h with the amount of Mg; (a) Mg 1.25 mol %, (b) 1.50 mol %, (c) 1.75 mol % and (d) 2.00 mol % (Si 1.5, Mn 0.2, Dy 0.75 mol %)

Fig. 5 displays results obtained from measuring changes in the dielectric constant depending on the measured temperature of the previously desribed microstructure specimens. Fig. 5(a), which is a result of the specimen seen in Fig. 3, shows dielectric properties related to the amount of Mg with the addition of Mn (0.2 mol %), Dy (0.75 mol %) and Si (1.0 mol %). Fig. 5(b), which is a result of the specimen seen in Fig. 4 shows

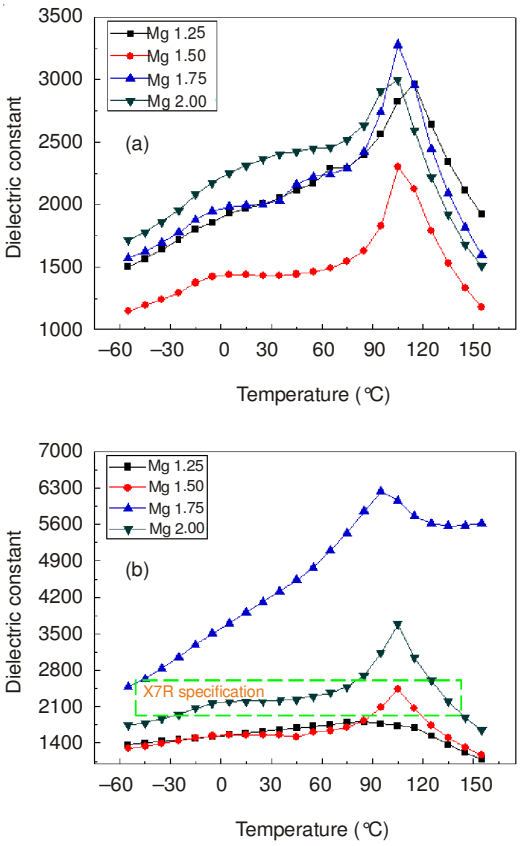

Fig. 5. Dielectric properties of the sintered $BaTiO_3$ at 1200 ℃ for 2 h with the amount of Si and Mg; (a) Si 1.0 mol % and (b) Si 1.5 mol % (Dy 0.75, Mn 0.2 mol %)

dielectric properties related to the amount of Mg with the addition of Mn (0.2 mol %), Dy (0.75 mol %) and Si (1.5 mol %). According to reports by Sakabe *et al.*[19] and Wang *et al.*[20], the dielectric constant changes depending on the grain size of $BaTiO_3$ dielectric material in a MLCC composition and the dielectric constant increases with increasingly greater grain size while it decreases with increasingly smaller grain size. As observed in the bulk density of Fig. 2 and in the microstructures of Figs. 4 and 5, the dielectric constant is found to generally increase with higher density and the dielectric constant of $BaTiO_3$ is found to have typical temperature dependence where the dielectric constant of phase transition sharply increases around the temperature where grains grow. However, no sequential increase of the dielectric constant related to the amount of added Mg ions is observed in Figs. 5(a) and (b). This result is presumed to be caused by the reflection of non-uniform grain dispersion into the dielectric properties due to different dispersions of grain size inside the microstructure. This non-uniform microstructure is ascribed to an insufficient amount or uneven distribution of liquid phase and it is necessary to ensure a uniform microstructure through additional additive experiments. Meanwhile, the composition with addition of 2 mol % Mg ions [Fig. 5(b)], is found to have a dielectric constant exceeding 2000 at room temperature, thereby approaching X7R temperature properties. Based on this result, further experiments should be conducted in the way of further adding Ba and Ca ions, previously known to act as a depressor and increasing the amounts of added Mg and Si, which are thought to be involved in the amount of liquid phase, so that grain growth and densification can be encouraged and eventually uniform microstructure can be secured.

Fig. 6 illustrates the microstructure of $BaTiO_3$ sintered at 1200 ℃ for 2 h, depending on changes in the composition of additives. Figs. 6(a) and (b) display the compositions with Ba and Ca added as a depressor, respectively and Fig. 6(c) and (d) show the microstructure of compositions with further addition of Si and Mg. As seen in these figures, Ba and Ca, which had been thought to work as a depressor when being added, are found to play roles in promoting grain growth. Based on this, the additives of Ba and Ca are expected to contribute to increasing the amount of liquid phase after being dissolved in the liquid phase. Also, according to Fig. 6(c), the grains are found to grow even when the amount of added Si ions increases. However, in the case of increasing the amount of added Mg ions, as seen in Fig. 6d, the observed densification and inhibited grain growth result in uniformly-sized particles, indicating that Mg ions perform well as an inhibitor of particle growth, as previously reported. Based on this result, it is thought that an insufficient amount of added Mg ions is involved in the creation of the liquid phase and thus contributes to improving grain growth and density while the Mg ions with a sufficient amount of liquid phase act as an inhibitor of grain growth. In the case of using $BaTiO_3$ with large-sized particles, the small specific surface area of the particles allowed the grain growth to be fully inhibited even with a small amount of liquid phase and added Mg ions. However, for 80 nm $BaTiO_3$, a larger amount of liquid phase and grain growth inhibitor should be added to make it possible to simultaneously control densification and microstructure in the case of large specific surface area of particles.

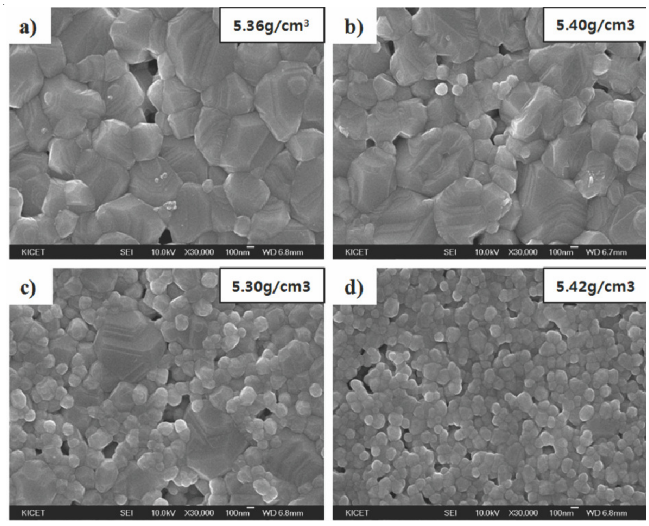

Fig. 6. Microstructures of sintered $BaTiO_3$ at 1200 ℃ for 2 h with the variation of additives; (a) Mn 0.2, Dy 0.75, Si 1.5 Mg 2.0 Ba 1.0 mol %, (b) Mn 0.2, Dy 0.75, Si 1.5 Mg 2.0 Ca 1.0 mol %, (c) Mn 0.2, Dy 0.75, Si 2.0 Mg 2.0 mol % and (d) Mn 0.2, Dy 0.75, Si 1.5 Mg 2.5 mol %

Fig. 7 displays results of observation of changes in dielectric properties related to each composition described in Fig. 6. As seen in the figure, the highest dielectric constant and low temperature stability were found in the Ba ion-added composition

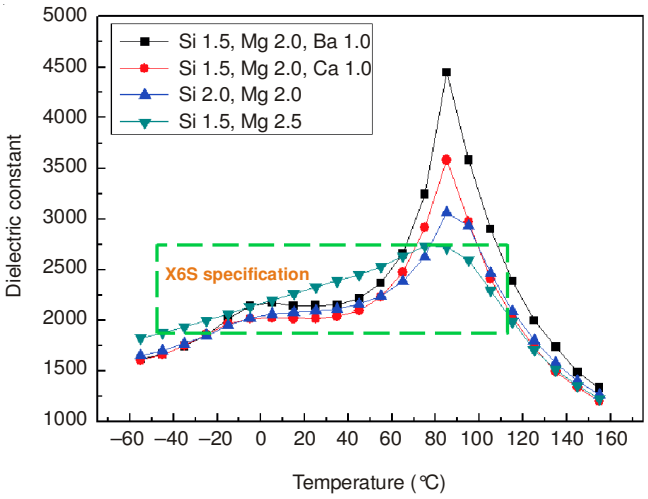

Fig. 7. Dielectric properties of the sintered $BaTiO_3$ at 1200 ºC for 2 h with the variation of additives (Mn 0.2, Dy 0.75)

having the biggest grain growth, in line with the microstructure. In addition, secured microstructure uniformity leads to temperature dependence of the dielectric constant, generally in good agreement with the trend of grain size seen in Fig. 6. In particular, in case of the composition with addition of 2.5 mol % Mg, the dielectric constant at room temperature surpassed 2000 and this satisfies the temperature properties of X6S, although it fails to satisfy the conditions of X7R.

Conclusion

Using $BaTiO_3$ powder of 80 nm average gain diameter, a variety of additives were coated with a liquid phase for MLCC composition development and the microstructure and dielectric properties depending on the amounts of Si and Mg ions added were observed as follows:

• Even when the amount of added Mg ions, known as an inhibitor of particle growth, was increased to 2 mol %, the grain growth was not inhibited and rather densification and grain growth were promoted further.

• For the composition with 2.5 mol % added Mg ions with a sufficient amount of liquid phase, the grain growth was inhibited and, accordingly, the dielectric properties met the conditions of X6S, reaching a dielectric constant of 2000 at room temperature.

• As a result of further addition of Ba and Ca ions able to work as a depressor, the temperature dependence of the dielectric constant was not improved while the grain growth was further promoted.

• In the study on MLCC dielectric composition using the 80 nm size $BaTiO_3$ material, it is concluded that the microstructure can be controlled only when a larger amount of liquid phase-forming agent and grain growth inhibitor are added as the specific surface area of the base material increases according to nanoparticle size.

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