The Korean Journal of Ceramice, **5**[3] 260-264 (1999)

Particle Size Effects on Microstructure Evolution and Microwave Dielectric Characteristics in $0.93MgTiO_3$-$0.07CaTiO_3$ Ceramics

Jung-A Lee, Jeong-Joo Kim, Nam-Kyoung Kim, Sang-Hee Cho and Jin-Woo Hahn*

Department of Inorganic Materials Engineering, Kyungpook National University, Taegu 702-701, Korea
**Electronics and Telecommunications Research Institute, Taejon 305-606, Korea*
(Received September 23, 1998)

Effect of the particle size of $MgTiO_3$ and $CaTiO_3$ on the microstructural evolution during sintering of $0.93MgTiO_3$-$0.07CaTiO_3$ system was investigated. Microwave dielectric characteristics of the sintered ceramics were also measured. The microstructural evolutions were explained with an emphasis on the entrapping behavior of $CaTiO_3$ grain into the $MgTiO_3$ grain and were correlated with microwave dielectric characteristics. With an increasing particle size ratio between $CaTiO_3$ and $MgTiO_3$, the fraction of entrapped $CaTiO_3$ grains increased, which grain growth of $MgTiO_3$ were concurrently accelerated due to decreasing drag force of its boundary migration. Besides, $CaTiO_3$-grain entrapment into the $MgTiO_3$ grain interior led to decreaseing quality factor values.

Key words : Microwave, Dielectric Properties, $0.93MgTiO_3$-$0.07CaTiO_3$ Microstructure, Particle Size

I. Introduction

Since the 1970's, microwave dielectric ceramics have been extensively studied in connection with the rapid progress in microwave telecommunication. It is well known that high dielectric constant (ε_r), high quality factor value (Q), and near zero temperature coefficient of resonant frequency (τ_f) are required for application of the microwave device. In practical use, it is important to adjust τ_f of the dielectric resonator to 0 ppm/°C. To adjust τ_f to zero, two or more compound having negative and positive τ_f values are employed to form a solid solution or mixed phases.

Two phase composites of $MgTiO_3$-$CaTiO_3$ have been popular for coaxial-type large-dimensional resonators.[1] Whereas $MgTiO_3$ has a high Q value of 22,000 (5 GHz), ε_r of 17, τ_f of −45 ppm/°C, those of $CaTiO_3$ are 170, 1,800 (5 GHz), and 800 ppm/°C, respectively. As $CaTiO_3$ has a much higher dielectric constant than $MgTiO_3$, $CaTiO_3$-containing phase even of a small amount, leads to an increase in ε_r, while the low Q value causes the Q values to drop.[2] It is also reported that composition of Mg:Ca≅ 93:7 has a τ_f value of nearly zero.[1] The dielectric constant of the $MgTiO_3$-$CaTiO_3$ material approximate well to the values predicted by a simple dielectric mixing rule.

In general, $MgTiO_3$ ceramics could readily be sintered to high densities at 1350°C~1400°C, with microstructures comprising a large amount of intragranular pores due to rapid grain growth.[2,3] During sintering of $MgTiO_3$-$CaTiO_3$ mixture, therefore $CaTiO_3$ phase was also frequently entrapped in the matrix grains of $MgTiO_3$ due to the rapid grain growth of $MgTiO_3$. Furthermore, $MgTiO_3$ and $CaTiO_3$ have different crystal structures. Consequently, each phase has no mutual solubility, so $CaTiO_3$ phase acts as a second phase.[4]

In this study, the effects of initial particle size ratio between $CaTiO_3$ and $MgTiO_3$ on the microstructural evolution of $0.93MgTiO_3$-$0.07CaTiO_3$ ceramics were studied, with an emphasis on the location of $CaTiO_3$ phase. Besides, microstructural characteristics and microwave dielectric properties are correlated.

II. Experimental Procedure

The starting materials were $MgTiO_3$ (High Purity Chemical Co., 99.9%) and $CaTiO_3$ (High Purity Chemical Co., 99% up) powders. To prepare coarse particles of $MgTiO_3$ and $CaTiO_3$, these powders were calcined at 1300°C for 2 and 10 h, respectively. Particle size and particle size distribution were measured by centrifugal particle size analyzer (SA-CP3, Shimadzu, Japan). Composition under study was selected to $0.93MgTiO_3$-$0.07CaTiO_3$ (by mole) of nearly zero temperature coefficient of resonant frequency. The powders were wet mixed for 16 h in distilled water, granulated, and cold-isostatically pressed at 100 MPa into cylindrical forms. These compacts were sintered at 1350°C for 2 h in air at a heating rate of 5°C/min.

Densities of sintered specimen were determined using an Archimedes method. For microstructural studies, specimens were ground on SiC, polished with diamond paste and thermally etched at 1300°C for 20 mins. The microstructures were observed using a scanning electron microscopy (SEM, JEOL-5400, Japan). Shrinkage and shrinkage rate of specimens during heating were measured using a vertical-loading dilatometer (Rigaku Thermoflex TMA 8140). Grain sizes of sintered specimen were deter-

mined using a linear intercept method.[5] Scanning electron microscopy (SEM) micrographs were taken in randomly selected areas of each specimen. The average grain size, G, was then calculated using the relation

$$G = \frac{1.5L}{MN}$$

where 1.5 is a geometry-dependent proportionality constant, L the total test line length, M the magnification and N the total number of intercept. While the fractions of $CaTiO_3$ particles were determined using a point counting method[5] and the same micrographs used for grain size measurement. The total number of particles on a micrograph was counted.

Microwave dielectric properties were determined at 6 GHz by the Hakki and Coleman method.[6]

III. Results and Discussion

Fig. 1(a) shows the particle size distribution of $MgTiO_3$ and $CaTiO_3$ powders. Fine $MgTiO_3$ and $CaTiO_3$ powders were as-received ones, whereas coarse $MgTiO_3$ and coarse $CaTiO_3$ were prepared by calcining at 1300°C for 2 and 10 h, respectively. The mean particle size of fine and coarse

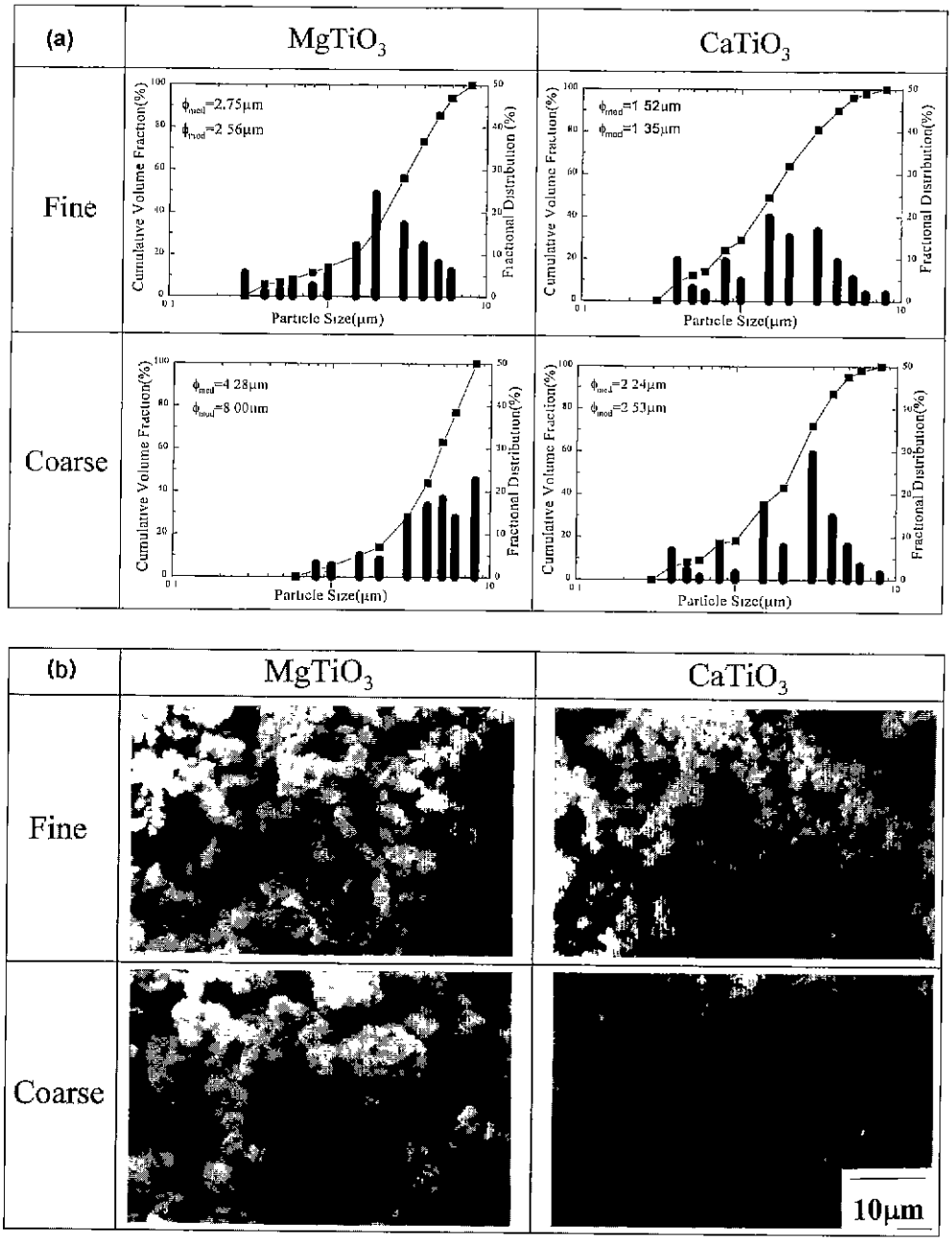

Fig. 1. (a) Particle size distribution and (b) SEM photomicrographs of $MgTiO_3$/$CaTiO_3$ fine/coarse powders.

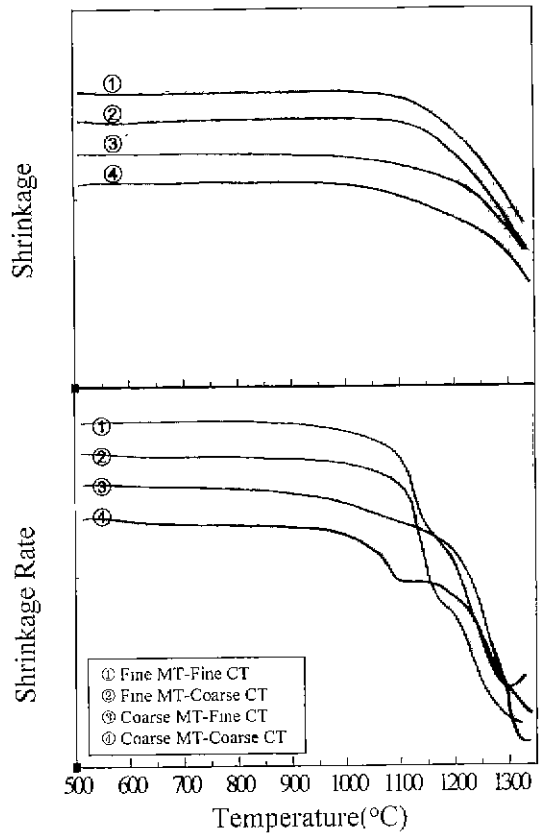

Fig. 2. Shrinkage and shrinkage rate of $0.93MgTiO_3$-$0.07CaTiO_3$ ceramics, as a function of particle ratios

$MgTiO_3$ was 2.75 and 4.28 μm, respectively. In the case of $CaTiO_3$, their mean values were 1.52 and 2.24 μm. The discrepancy of the median and the modal diameter of $MgTiO_3$ powder was larger than that of $CaTiO_3$, which

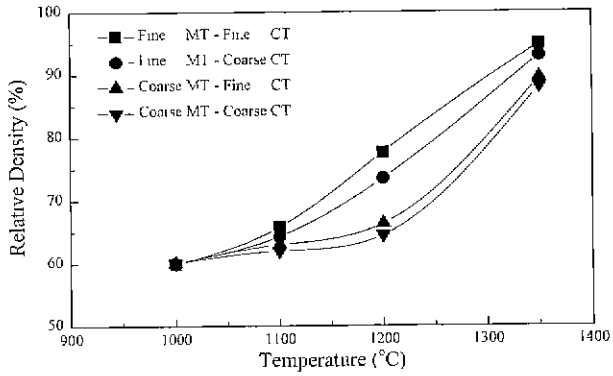

Fig. 3. Density versus sintering temperatures of 0.93 $MgTiO_3$ -0.07$CaTiO_3$ ceramics.

indicates that $MgTiO_3$ particles grew abnormally during the calcination process, even though the former was calcined for a shorter time (2h). Moreover the size distributions of $MgTiO_3$ powders were somewhat broader than those of $CaTiO_3$ powders. Fig. 1(b) shows SEM photographs of the fine and the coarse powders, where the morphologies and extents of agglomeration were not much different.

Shrinkage and shrinkage rate of $MgTiO_3$-$CaTiO_3$ specimens are plotted in Fig. 2. As the particle size of $MgTiO_3$, which is a matrix part, was finer, the shrinkage process seems to have been accelerated. Meanwhile the particle size of $CaTiO_3$, which was a minor part, did not affect seriously on the densification behavior. It is well known that small particles undergo faster densification than the larger ones.[7] It is of interest to note that all specimens except the coarse $MgTiO_3$-fine $CaTiO_3$ case showed a node in the shrinkage rate curve.

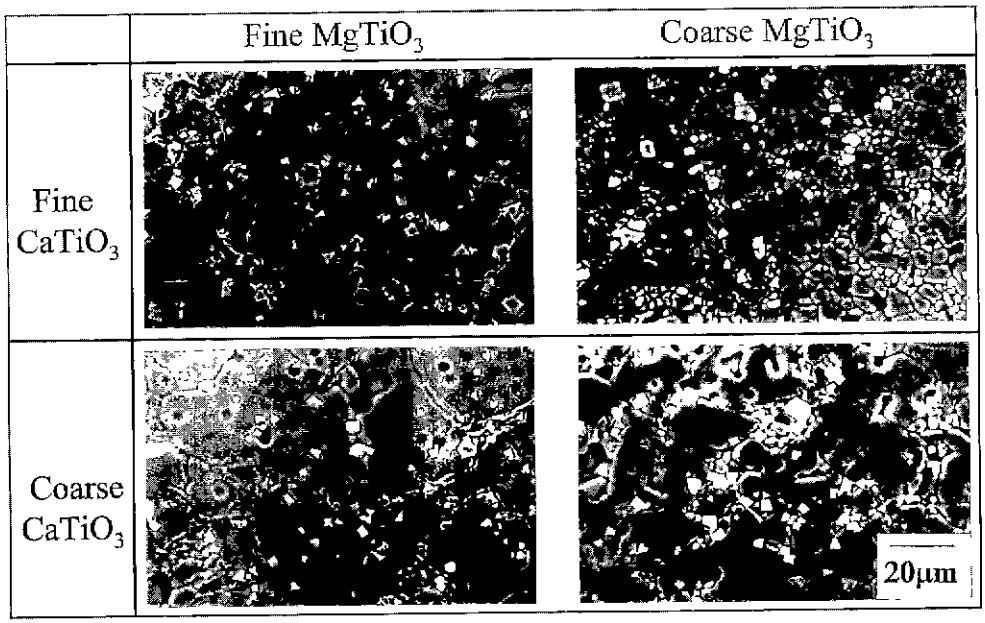

Fig. 4. Microstructures of $0.93MgTiO_3$-$0.07CaTiO_3$ ceramics sintered at 1350°C for 2 h.

Table 1. Ratio of Initial Particle Size between $CaTiO_3$ and $MgTiO_3$ and $CaTiO_3$ Fraction of 0.93 $MgTiO_3$-0.07$CaTiO_3$ System

Powder characteristics	Particle size ratio $[r_{CaTiO_3}/r_{MgTiO_3}]$	$CaTiO_3$ phase fraction in the grain interior (sintered at 1350°C for 2h)
Fine MT-Fine CT	0.55	23.6%
Fine MT-Coarse CT	0.81	44.9%
Coarse MT-Fine CT	0.36	1.2%
Coarse MT-Coarse CT	0.52	14.5%

Fig. 3 illustrates the density variation of 0.93$MgTiO_3$-0.07$CaTiO_3$ specimens sintered at indicated temperatures for 2 h. In the case of fine $MgTiO_3$ powders, the densities increased gradually with increasing sintering temperatures. Densification started above 1200°C, when the coarse $MgTiO_3$ powders were used. The overall densities of the sintered specimens were higher in the fine $MgTiO_3$ cases.

Fig. 4 shows the microstructures of 0.93$MgTiO_3$-0.07 $CaTiO_3$ specimens sintered at 1350°C for 2 h. Except for the coarse $MgTiO_3$-fine $CaTiO_3$ case, considerable amounts of $CaTiO_3$ grains and pores were entrapped into the interior of $MgTiO_3$ grains. The grain size of $MgTiO_3$ and $CaTiO_3$ were 29.2 and 3.4, 33.9 and 4.3, 11.0 and 2.4, and 15.9 and 3.1 μm, for the four cases. The grain sizes of $CaTiO_3$ phase were close, regardless of the specimen. In a coarse $MgTiO_3$-fine $CaTiO_3$ specimen, $MgTiO_3$ grain are small and $CaTiO_3$ particles are located on the grain boundaries, which indicated the pinning of $MgTiO_3$ grain boundaries by the $CaTiO_3$ particles. In such a case, the $CaTiO_3$ particles inhibited the grain growth of the $MgTiO_3$ matrix significantly.

Table 1 summarizes the ratio of the initial particle size and fraction of $CaTiO_3$ on the grain boundary in the specimens. The fine $MgTiO_3$-fine $CaTiO_3$ specimen shows the particle size ratio of 0.55 and the $CaTiO_3$ fraction of 23.6%, but the values of 0.36 and 1.2% were obtained in the coarse $MgTiO_3$-fine $CaTiO_3$ specimen. It was suggested that a decrease in particle size ratio led to an inhibition of grain growth of $MgTiO_3$. As mentioned above, $MgTiO_3$-$CaTiO_3$ system could be considered as two-phase composites. Stearn et al. investigated the particle-inhibited grain growth in Al_2O_3-SiC composites and found that the amount of second phase on the grain boundary decreased the grain growth rate.[8,9] Larger volume fractions of particles and smaller inclusion size were more effective in pinning the boundaries with increased volume fraction, predicted by an equilibrium Zener's model.[10]

$$G_L = \frac{4r}{3f}$$

where G_L, r and f are the limiting grain size, radius of the inclusion, and particle volume fraction, respectively.

Therefore, with increasing the initial particle size of $CaTiO_3$ phase, the role of $CaTiO_3$ as pinning sources became difficult, the grain growth of $MgTiO_3$ accelerated,

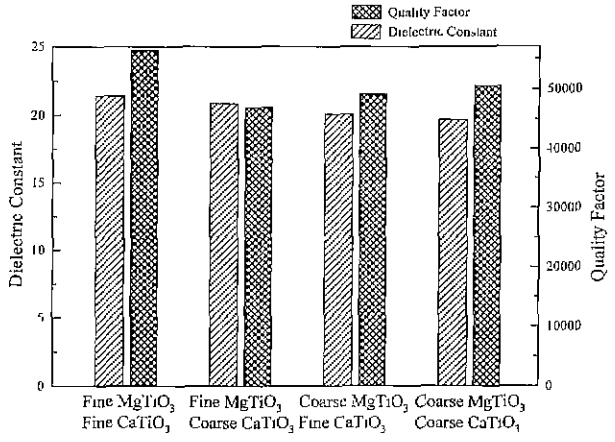

Fig. 5. Microwave dielectric constant and quality factor of 0.93$MgTiO_3$-0.07$CaTiO_3$ ceramics as a function of powder characteristics.

and then fractions of entrapped $CaTiO_3$ increased drastically. On the contrary, $CaTiO_3$ grains were located in the grain boundary in the coarse $MgTiO_3$-fine $CaTiO_3$ system. It was explained preciously that fine $CaTiO_3$ particles pinned the boundary effectively and furthermore the driving force for grain growth was also small due to large grain size of $MgTiO_3$ phase. Besides, the node in shrinkage rate curve, Fig. 2, seems to be related with entrapping $CaTiO_3$ grains into the $MgTiO_3$ grain interior. It was suggested that each inclusion inside the composite constitutes a nodal work and the relative displacement of each inclusion determined the shrinkage strain.[11] The apparent bulk shrinkage is the summation of the constrained strain between nodal point. Therefore, the shrinkage node seems to have arisen when $CaTiO_3$ was entrapped into the $MgTiO_3$ grain.

Fig. 5 shows microwave dielectric constants and quality factors. As shown fine $MgTiO_3$-fine $CaTiO_3$ specimen, with the highest relative density, showed highest dielectric constant of 21.5, whereas the low density specimen, coarse $MgTiO_3$-coarse $CaTiO_3$, revealed low dielectric constant of 19.7, inferring close relationship between dielectric constant and relative density.

In the quality factor, the value of 46,950 in fine $MgTiO_3$-coarse $CaTiO_3$ system was the lowest, where the fraction of entrapped $CaTiO_3$ grain was highest. It is well known that various lattice defects containing lattice distortions and imperfections deteriorate Q value in the microwave dielectric materials.[12-15] In two phase composites as $MgTiO_3$-$CaTiO_3$ system, stress might be built up due to difference of thermal expansion coefficient between the two phase, which lead to lattice distortion.[11,16] Especially, as $CaTiO_3$ grain entrapped into the $MgTiO_3$ grains increased, it was more difficult to reveal this strain compared with locating in grain boundary. Consequently, entrapping of $CaTiO_3$ grains led to lattice distortion and quality factor decreased concurrently.

IV. Summary

Effect of the initial particle size of $MgTiO_3$ and $CaTiO_3$ on the microstructural evolution during the sintering of $MgTiO_3$-$CaTiO_3$ composite system was studied and composed with microwave dielectric characteristics. When fine $MgTiO_3$ powder was used, densification was promoted and resulted in dielectric constant increase. The microstructure evolution in the $MgTiO_3$-$CaTiO_3$ system was interpreted by the pinning effect of $CaTiO_3$ particle in the grain boundary. With an increase in initial particle size ratio between $CaTiO_3$ and $MgTiO_3$, the pinning force of $CaTiO_3$ at the boundary was decreased and the fraction of entrapped $CaTiO_3$ grain into the $MgTiO_3$ grain interior was increased, which led to decrease in quality factor.

Acknowledgments

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997.

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