Journal of the Korean Ceramic Society
Vol. 39, No. 3, pp. 222~225, 2002.

Strain Analysis for Quality Factor of the Layered $Mg_{0.93}Ca_{0.07}TiO_3$ -$(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ Ceramics at Microwave Frequencies

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(Received February 28, 2002; Accepted March 14, 2002)

ABSTRACT

Microwave dielectric properties of the layered and functionally graded materials (FGMs) of $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT) with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST) were investigated as a function of the volume ratio of two components. Dielectric constant was decreased with an increase of the volume ratio of MCT which had a lower dielectric constant than CLST. For the layered FGMs specimens, the difference of thermal expansion coefficients between two components induced thermal strain to dielectric layers, which was confirmed by the plot of Δk (X-ray diffraction peak width) versus k (scattering vector) using the double-peak Lorentzian function, $f(x)$. Quality factor of the specimens was affected by the thermal strain of dielectric layer, especially MCT layer. For the specimen with the volume ratio of MCT/CLST = 2, the quality factor of the specimen showed a minimum value due to the maximum thermal strain of MCT layer.

***Key words :** $Mg_{0.93}Ca_{0.07}TiO_3$, $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$, Quality factor, Thermal strain, Diffraction peak width Δk*

1. Introduction

The demand for microwave dielectric resonators is rapidly rising as communication systems depend on the advance in microwave technologies. With advances in the technology, there is a continuous propel toward higher levels of system integration and miniaturization, and many interests and researches have been paid attention in recent years to the development of new technologies for designing a multilayer composite and a compositional gradient layer.[1-3] A functionally graded materials (FGMs) technology is one of good solutions for this demand.[4] However, the induced thermal strain and stress are inevitable for each layer of the FGMs structure if FGMs are composed of materials with quite different thermal properties.

Generally, thermal strain and stress can cause the structural and electrical failures,[5] and this strain is a very important factor influencing the dielectric properties of materials. For the multilayer structure specimens, the induced stress arose from several contributions such as the lattice mismatch and the difference in the thermal expansion coefficients between the component materials.[6] And it was reported that the reduction of thermal strain in the thin films resulted in the decrease in dielectric quality factor.[7] Therefore, the effect of induced strain on the properties of FGMs should be studied to enhance the properties associated with their applications.

In this work, the layered FGMs structure of $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT) with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST), which resulted in a stepwise gradient, was prepared and the effect of strain on quality factor of the layered FGMs specimens was studied as a function of the volume ratio of its components. To investigate the dependence of quality factors on the induced strains of each layer in FGMs structure, the thermal strains applied to dielectric layers were estimated from the change of X-ray diffraction peak widths Δk as a function of scattering vector k using the double-peak Lorentzian function $f(x)$.[7,8]

2. Experimental

MgO, $CaCO_3$, TiO_2, Li_2CO_3, and Sm_2O_3 with purity higher than 99.5% were used as starting materials. They were batched to the desired composition and then wet mixed for 24h in ethanol and then dried. The reagents were calcined at 1000°C for 2 h for $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST) and 1100°C for 4 h for $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT), respectively. Prepared powders were pressed uniaxially in a layered FGMs structure at 1000 kg/cm^2 and cold isostatic pressed at 1450 kg/cm^2. These pellets were sintered at 1350°C for 3 h in air. Fig. 1 shows the schematic diagrams of the layered FGMs specimens of MCT with CLST. The volume ratio of MCT/CLST was varied from 1 to 3, and each specimen was denoted to M-C, 2M-C and 3M-C, respectively.

Crystalline phases of the sintered specimens were identified by an X-ray powder diffraction (Rigaku D/Max-3C, Japan) using Cu Kα radiation (λ=1.54 Å) with 40 kV/30 mA, sampling width of 0.02°, and scan speed of 4°/min in the 2θ range of 20-80°. For the strain analysis, X-ray diffraction

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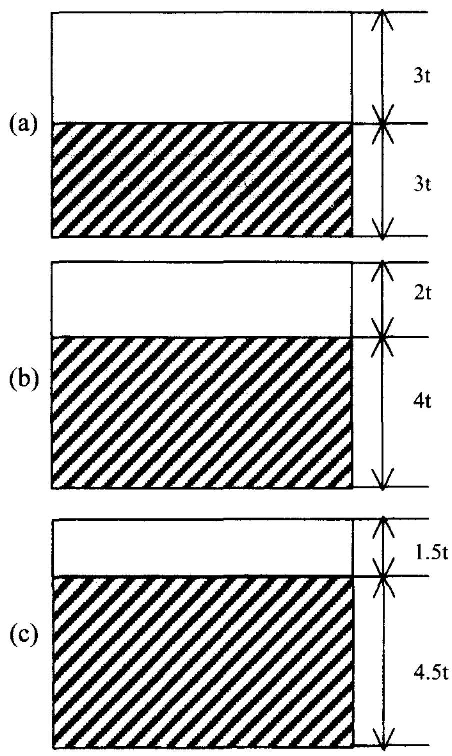

Fig. 1. Schematic diagrams of layered FGMs structures of $Mg_{0.93}Ca_{0.07}TiO_3$ and $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics; (a) M-C, (b) 2M-C and (c) 3M-C specimens. (▨: $Mg_{0.93}Ca_{0.07}TiO_3$, □: $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$)

peak widths, Δk (FWHM) were fitted for each peak with the scattering vector $k=(4\pi/\lambda)\sin\theta$, using a double-peak Lorentzian function for the quantitative estimation of the strain of the dielectric layers, considering the effect of $K\alpha_1$ and $K\alpha_2$, and instrumental broadening effect.[7,8] Microwave dielectric properties were measured by the post resonant method with the TE_{011} mode.[9]

3. Results and Discussion

X-ray diffraction patterns of pure MCT and CLST, and the interfaces of the layered FGMs specimens with two components sintered at 1350°C for 3 h were shown in Fig. 2. For MCT, the mixture of $MgTiO_3$ and $CaTiO_3$ were detected. It was reported that $CaTiO_3$ phase did not form a solid solution with matrix phase $MgTiO_3$ and settled at triple points between $MgTiO_3$ grains.[10,11] For CLST, however, a complete solid solution of $CaTiO_3$-type perovskite phase was observed. For all the layered FGMs specimens, the mixture of $MgTiO_3$ and $CaTiO_3$-type perovskite was observed and neither secondary phase nor compound of them was found at the interface of two systems.

Table 1 shows the dielectric properties of pure MCT and CLST, and the layered FGMs specimens at microwave frequencies range. For the layered FGMs specimens, dielectric constant showed an intermediate value between two components for the M-C specimen, and decreased with an increase

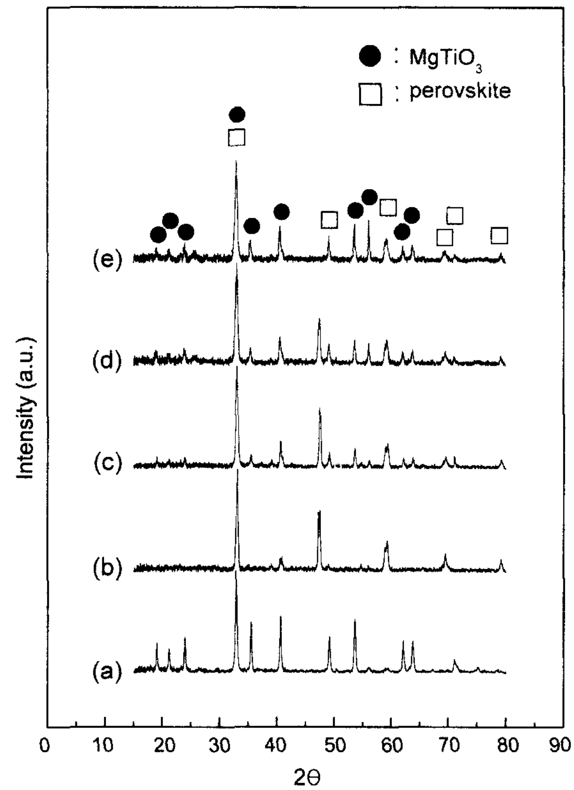

Fig. 2. XRD patterns of (a) $Mg_{0.93}Ca_{0.07}TiO_3$ and (b) $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics, and their interfaces of layered FGMs structure sintered at 1350°C for 3 h; (c) M-C, (d) 2M-C, and (e) 3M-C specimens, respectively.

Table 1. Microwave Dielectric Properties of $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT) with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST) Ceramics and the Layered FGMs Specimens Sintered at 1350°C for 3 h

	MCT	CLST	M-C	2M-C	3M-C
Dielectric constant	22.15	92.12	73.97	58.76	35.59
Quality factor	68551	8262	7897	6597	6970

of the volume ratio of MCT. These results were due to the lower dielectric constant of MCT ($k \approx 22$) than that of CLST ($k \approx 92$). However, quality factor of the layered FGMs specimens did not depend on the volume ratio of each component. The M-C specimen showed the highest quality factor, while the 2M-C specimen showed the lowest quality factor. Thermal expansion coefficients of pure MCT and CLST measured by thermomechanical analysis (TMA) were 7.846×10^{-6}/°C and 8.845×10^{-6}/°C, respectively, and this difference between two components could cause thermal strain in each dielectric layer during the cooling down process after sintering.[6]

For the quantitative estimation of the thermal strains of the layered FGMs specimens, the X-ray diffraction peak widths Δk (full width at half maximum: FWHM) were fitted at various stages for each peak as a function of the scattering vector $k=(4\pi/\lambda)\sin\theta$.[12,13] To consider unresolved $K\alpha$, and

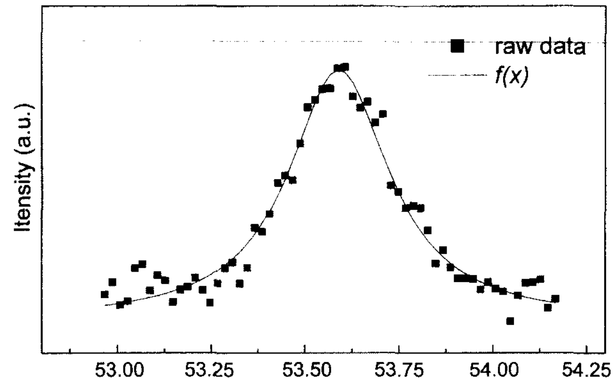

Fig. 3. Double-peak Lorentzian fitting using *f(x)* as a fitting function (peak intensity=65, FWHM=0.163, $K\alpha_1$ peak position=53.59). The X-ray diffraction patterns were from the layered FGMs M-C specimen of $Mg_{0.93}Ca_{0.07}TiO_3$ with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics sintered at 1350°C for 3 h.

$K\alpha_2$ peaks with the instrumental broadening effect, the double-peak Lorentzian function, *f(x)*, was used in obtaining the true peak widths Δk by the separation of the $K\alpha_1$ and $K\alpha_2$ peaks as shown in Fig. 3.

$$f(x) = \frac{I\omega}{(x-x_0)^2+\omega^2} + \frac{0.5I\omega}{(x-x_0')^2+\omega^2} + b$$

where I : intensity
ω : full width at half maximum
x : peak position for $K\alpha_1$,
x_0 : peak position for $K\alpha_2$, $\left(x_0' = 2\sin^{-1}\left(\frac{\lambda_{k\alpha_2}}{\lambda_{k\alpha_1}}\sin\frac{x_0}{2}\right)\right)$
b : background

assuming that the FWHM (ω) of each peak due to $K\alpha_1$ and $K\alpha_2$ have the same value. The instrumental broadening effect is then subtracted using the resolution function estimated from the diffraction pattern of a standard silicon powder. In addition, Δk is known to have a relation with strain and grain size as follows:

$$\Delta k = \frac{\Delta d}{d}k + K\frac{2\pi}{D}$$

where, $(\Delta d/d)$ is the strain of the specimens and D is the effective grain size suggested by Scherrer with the shape factor K.[8] From this relation, the strain of the specimens can be estimated from the slope of the plot of Δk versus k after correction by the resolution function ($\Delta k_{resolution}$=0.07656 (±0.0038)+0.00192 (±0.000085)k) as shown in Fig. 4. The error ranges in Fig. 4 are from the double-peak Lorentzian fitting for the X-ray diffraction peaks.[8]

Table 2 shows the estimated strains from the slope of Δk vs. k plots for the layered FGMs specimens sintered at 1350°C for 3 h. The strains applied to each dielectric layer were corrected by the resolution function. In a multilayer structure ceramics, each component might be sintered at different temperatures and shrank differently. However,

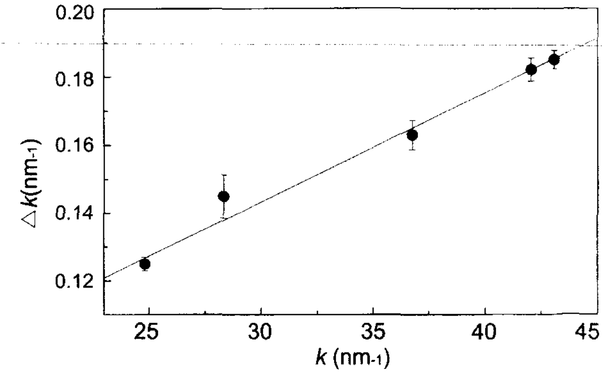

Fig. 4. Typical Δk vs. k plot for the layered FGMs M-C specimen of $Mg_{0.93}Ca_{0.07}TiO_3$ with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics sintered at 1350°C for 3 h ; $\Delta k = 2\pi/D + (\Delta d/d)\,k$ = (0.024 ±0.005) + (0.00115±0.000017) k.

Table 2. Estimated Strains from the Slopes of Δk vs. k Plots for the Layered FGMs Specimens of $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT) with $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST) Ceramics Sintered at 1350°C for 3 h

		M-C	2M-C	3M-C
Estimated Strains	MCT layer	0.00115 (±0.00017)	0.00271 (±0.00183)	0.00159 (±0.0010)
	CLST layer	0.00781 (±0.00031)	0.00838 (±0.00232)	0.01010 (±0.0025)

($\Delta k_{resolution}$=0.07656 (±0.0038)+0.00192 (±0.000085)k)

these induced thermal strains could be assumed to be relaxed due to creep at the sintering temperature.[14] Therefore, thermal strains applied to dielectric layers of FGMs could be assumed to arise only from the difference in thermal expansion coefficients between two components during the cooling down process after sintering.

With an increase of the volume ratio of MCT, total contraction of layered FGMs specimens during the cooling down process was much affected by the thermal contraction of MCT, and the thermal stress was concentrated on the relatively thin CLST layer. Therefore, the thermal strain applied to CLST layer increased with an increase of volume ratio of MCT, and the largest strain was obtained in the 3M-C specimen. On the other hand, thermal strain of MCT layer showed a maximum value in the 2M-C specimen and then decreased in the 3M-C specimen as shown in Table 2. The increased displacement of CLST layer could cause an increase in the strain of MCT, and for the 2M-C specimen, the quality factor decreased remarkably due to the increase of thermal strains of MCT and CLST layers. For the 3M-C specimen, however, the MCT layer was thick enough not to be affected by the increased strain of CLST layer, and the strain of MCT showed lower value than 2M-C specimen. Quality factor of the 3M-C specimen, in turn, increased slightly due to the decreased thermal strain of MCT layer, in spite of the high thermal strain of CLST. From the results shown in Table 1 and Table 2, it could be implied that the dielectric properties of layered FGMs structure specimens were controlled by the change in volume ratio of each dielectric layer and quality factor of the specimens was related with the induced thermal strain of each dielectric layer, especially the strain of MCT layer.

4. Conclusion

As the volume ratio of MCT increased, dielectric constant of the layered FGMs specimens decreased and the 3M-C specimen showed a minimum value of about 35.5. However, quality factor of the specimens was not depended on the volume ratio of dielectric layer. As the volume ratio of MCT increased, thermal strain applied to CLST layer increased. On the other hand, thermal strain applied to MCT layer showed a maximum value in the 2M-C specimen for which the lowest quality factor was obtained. Therefore, the dielectric properties of layered FGMs structure specimens could be optimized by the control of volume ratio of each dielectric layer, and the change in quality factor of the layered FGMs specimens was attributed to the thermal strain of dielectric layer, especially, MCT layer.

Acknowledgement

This work was supported by the Brain Korea 21 project.

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