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Microwave dielectric properties of $MgTiO_3$–$SrTiO_3$ layered ceramics

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Abstract

$MgTiO_3$–$SrTiO_3$ layered ceramics with different stacking were fabricated and the microwave dielectric properties were evaluated with TE_{011} mode. With increasing $SrTiO_3$ thickness fraction, the resonant frequency (f_0) decreased, while the effective dielectric constant ($\varepsilon_{r,\mathrm{eff}}$) and temperature coefficient of resonant frequency (τ_f) increased for the bi-layer ceramics. The stacking arrangement also had significant effect on the microwave dielectric properties. For the same $SrTiO_3$ thickness fraction of 0.333, the tri-layer $MgTiO_3$/$SrTiO_3$/$MgTiO_3$ ceramics had lower f_0, higher $\varepsilon_{r,\mathrm{eff}}$ and τ_f. The result was not consistent with the previous report on the layered ceramics with TE_{011} mode [Cho, J. Y., Yoon, K. H. and Kim, E. S., Effect of stress on microwave dielectric properties of layered $Mg_{0.93}Ca_{0.07}TiO_3$–$(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics. *Mater. Chem. Phys.* 2003, **79**, 286; Cho, J. Y., Yoon, K. H. and Kim, E. S., Correlation between arrangement of dielectric layers and microwave dielectric properties of $Mg_{0.93}Ca_{0.07}TiO_3$–$(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ ceramics. *J. Am. Ceram. Soc.* 2003, **86**, 1330], where the effective dielectric constant was only determined by the thickness fraction and was independent of the stacking arrangement. Finite element analysis gave an explanation for the different microwave dielectric behaviors of the bi- and tri-layer ceramics in the present experiment.
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Keywords: Composites; Interfaces; Dielectric properties; Finite element method; $MgTiO_3$; $SrTiO_3$

1. Introduction

Dielectric ceramics have been widely used for microwave applications as dielectric resonators and the main requirements for the ceramics are high dielectric constant, high Qf value and near-zero temperature coefficient of resonant frequency.[1–3] However, many ceramics cannot meet these requirements simultaneously and their properties need to be tuned.[1–3] Layered ceramics were introduced to tune the microwave dielectric properties as a new approach.[4–7] By stacking one dielectric ceramic with positive temperature coefficient of resonant frequency with another ceramic which has a negative one, the near-zero temperature coefficient could be obtained without damaging the Qf value much.[4–7] Also, the impedance-stepped resonator as a new type of microwave resonator for shorter resonant length and various applications promoted the research on the layered ceramics.[8–11] However, the microwave dielectric behaviors of the layered ceramics and the mechanisms have not been understood deeply and they are worthy of further investigating.

$MgTiO_3$ and $SrTiO_3$ are well-known microwave dielectric ceramics with opposite temperature coefficients of resonant frequency, and the formation of solid solution between them is impossible for the incompatibility in crystal structure and the large difference between the ionic radiuses of Mg^{2+} and Sr^{2+}. The multiphase ceramics they form indicate high dielectric loss. It is an alternative method to laminate $MgTiO_3$ with $SrTiO_3$ to tune the microwave dielectric properties. In the present work, the effects of $SrTiO_3$ thickness fraction and stacking arrangement upon the microwave dielectric properties of the layered ceramics with TE_{011} mode are discussed, and the resonant frequency and effective dielectric constant are predicted by finite element method.

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2. Experimental procedure

$MgTiO_3$ and $SrTiO_3$ powders were synthesized by a solid-state reaction process. MgO (97%), $SrCO_3$ (99.95%) and TiO_2 (99.5%) raw powders with the proper ratios were mixed by ball milling in distilled water with zirconia media for 24 h and then calcined at 1100 °C in air for 3 h to synthesize $MgTiO_3$ and $SrTiO_3$, respectively. The $MgTiO_3$ and $SrTiO_3$ powders with organic binder of 5% PVA water solution were pressed into layered cylindrical compacts with various stacking. These compacts were sintered at 1350 °C in air for 3 h. After cooling from the sintering temperature to 1100 °C at a rate of 1 °C/min, the ceramics were naturally cooled inside the furnace.

Scanning electron microscopy (SEM) observations were taken on the fractured surface of the layered ceramics. The resonant frequency and Qf value were evaluated at room temperature with TE_{011} mode using the paralleling plate method.[12] The temperature coefficient of resonant frequency was determined between 20 and 80 °C with the same resonant mode. The effective dielectric constant was calculated according to the diameter (*D*) and thickness (*H*) of the sample and the resonant frequency (f_0) by Eq. (1):

$$\varepsilon_{r,\mathrm{eff}} = \left(\frac{\alpha_1 c}{2\pi D f_0}\right)^2 + \left(\frac{c}{2Hf_0}\right)^2, \tag{1}$$

where c is the light speed in free space and α_1 is a first root of the characteristic equation.[12]

3. Finite element analysis

The axis symmetry exists for TE_{011} mode and the electric field only has a rotational component E_θ that is also axis symmetrical, so two-dimensional finite element method can be used to analyze the layered ceramics and only half of the cross section needs to be analyzed. Only the space within 25.3 mm far from the symmetry axis is considered since the electromagnetic energy concentrates in and near the sample and the space far from the sample can be neglected. The analyzed area is divided into 277 × 144 rectangles, as shown in Fig. 1, and then each rectangle is divided into two triangles along the diagonal from the bottom left corner to the top right corner. Thus, 278 × 145 nodes and 2 × 277 × 144 triangular first-order elements are attained for the following analysis.

For TE_{011} mode, E_θ satisfies the Helmoltz equation:

$$\frac{\partial^2 E_\theta}{\partial r^2} + \frac{\partial^2 E_\theta}{\partial z^2} + \frac{1}{r}\frac{\partial E_\theta}{\partial r} + \left((2\pi f_0)^2 \mu\varepsilon - \frac{1}{r^2}\right)E_\theta = 0, \tag{2}$$

where f_0 is the resonant frequency.

Using Galerkin weighted residual approach and letting $E_\theta = rE$,[13,14] Eq. (2) can be rewritten as:

$$\int_S \left[\frac{\partial^2 rE}{\partial r^2} + \frac{\partial^2 rE}{\partial z^2} + \frac{1}{r}\frac{\partial rE}{\partial r} + \left((2\pi f_0)^2 \mu\varepsilon - \frac{1}{r^2}\right) rE\right] \times rw\,dS = 0, \tag{3}$$

where w is the weighting function. From Eq. (3), the matrix equation of each element can be expressed as:

$$[a - (2\pi f_0)^2 b][E] = 0, \tag{4}$$

where a and b are 3 × 3 matrices that can be calculated from the coordinates for each node.[13,15]

Assembling the matrix equations of all the elements and introducing the condition of $E_\theta = 0$ for the nodes on the boundary of the analyzed area, the overall matrix equation can be obtained as:

$$[A^* - (2\pi f_0)^2 B^*][E^*] = 0. \tag{5}$$

This equation set has innumerable solutions corresponding to TE_{0np} resonant modes, and the solution with the lowest resonant frequency corresponds to TE_{011} mode. It can be easily attained with a personal computer. Also, the electric field intensity for each node is attained from E^*, so that the contour of the electric field intensity can be plotted.

4. Results and discussion

Table 1 shows the experimental parameters for the $MgTiO_3$–$SrTiO_3$ layered ceramics in the present work. The average diameter and total thickness for all the ceramics are about 10.60 and 5.00 mm, respectively. The SEM photograph on the fractured surface is shown in Fig. 2, and the smooth

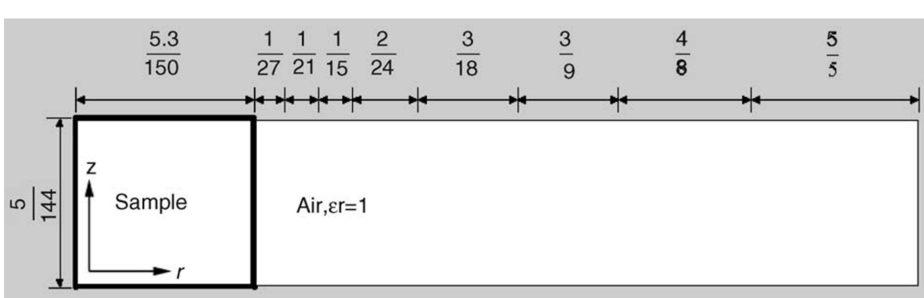

Fig. 1. Half of the cross section for finite element analysis, where the fractional number (*n*/*m*) denotes that the length is *n* mm and divided into *m* segments averagely.

Table 1
Experiment parameters for the $MgTiO_3$–$SrTiO_3$ layered ceramics

Stacking arrangement	Thickness ratio				
$MgTiO_3/SrTiO_3$	3:1	2:1	1:1	1:2	1:3
$MgTiO_3/SrTiO_3/MgTiO_3$		1:1:1			
Thickness fraction of $SrTiO_3$	0.25	0.333	0.5	0.667	0.75

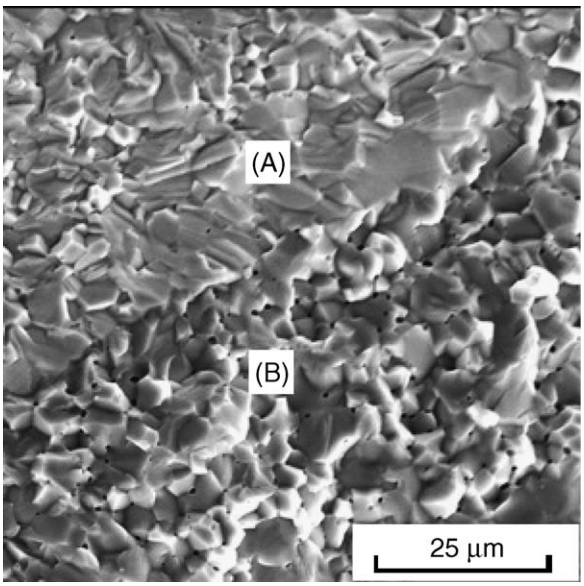

Fig. 2. SEM photograph of the fractured surface of the $MgTiO_3$–$SrTiO_3$ layered ceramics ((A) $SrTiO_3$; (B) $MgTiO_3$).

$MgTiO_3$–$SrTiO_3$ interface with close bond is observed. The EDS results also indicate that no distinct diffusion occurs near the interface.

Figs. 3 and 4 show the experimental resonant frequency and effective dielectric constant of the layered $MgTiO_3$–$SrTiO_3$ ceramics with TE_{011} mode as function of $SrTiO_3$ thickness fraction, as the solid points indicate. With increasing $SrTiO_3$ thickness fraction, the resonant frequency decreases and the effective dielectric constant increases for the bi-layer $MgTiO_3/SrTiO_3$ ceramics. The stacking arrangement also has significant effect on the resonant frequency and effective dielectric constant. For the same $SrTiO_3$ thickness fraction of 0.333, the tri-layer $MgTiO_3/SrTiO_3/MgTiO_3$ ceramics (with thickness ratio of 1:1:1) has lower resonant frequency and higher effective dielectric constant than the bi-layer $MgTiO_3/SrTiO_3$ ceramics (with thickness ratio of 2:1). However, according to the results for the $Mg_{0.93}Ca_{0.07}TiO_3$–$(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ layered ceramics reported by Cho et al.,[10,11] the effective dielectric constant with TE_{011} mode is only determined by the thickness fraction and does not change significantly with the stacking arrangement. The different results will be discussed in the later paragraph.

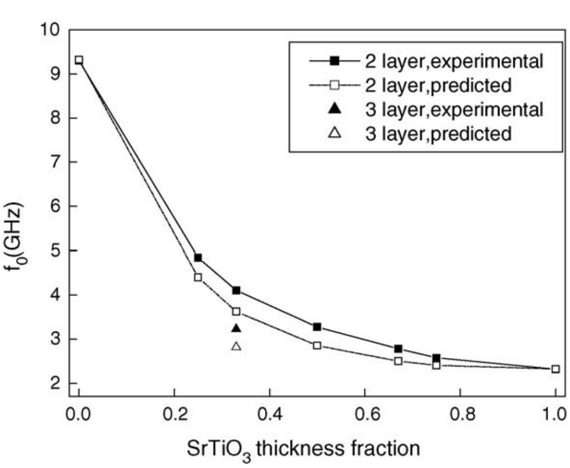

Fig. 3. Resonant frequency of the $MgTiO_3$–$SrTiO_3$ layered ceramics with TE_{011} mode (experimental and predicted by finite element method).

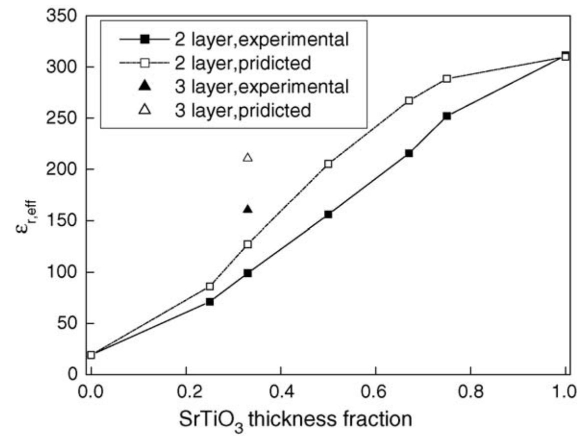

Fig. 4. Effective dielectric constant of the $MgTiO_3$–$SrTiO_3$ layered ceramics with TE_{011} mode (experimental and predicted by finite element method).

Finite element method can give an explanation for the different behaviors between the bi- and tri-layer ceramics in the present work. Fig. 5a and b show the simulated contours of the electric field intensity with the relative intensity marked for the bi-layer $MgTiO_3/SrTiO_3$ ceramics with thickness ratio of 2:1 and the tri-layer $MgTiO_3/SrTiO_3/MgTiO_3$ ceramics with thickness ratio of 1:1:1. The $SrTiO_3$ thickness fractions are all 0.333, but the contours are quite different. The tri-layer ceramics has symmetric electric field distribution along the thickness direction and the field focuses in $SrTiO_3$ layer, while the electric field is asymmetric for the bi-layer ceramics and weaker electric field distributes in $SrTiO_3$ layer. That is, $SrTiO_3$ layer contributes more to the final microwave dielectric properties for the tri-layer ceramics than for the bi-layer ceramics. Also, $SrTiO_3$ has much higher dielectric constant than $MgTiO_3$, so the resonant frequency is lower and the effective dielectric constant is higher for the tri-layer ceramics comparing with the bi-layer ceramics, as the experiment indicates.

The predicted resonant frequency and effective dielectric constant of the layered ceramics by finite element method are also shown in Figs. 3 and 4, as the hollow points indicate.

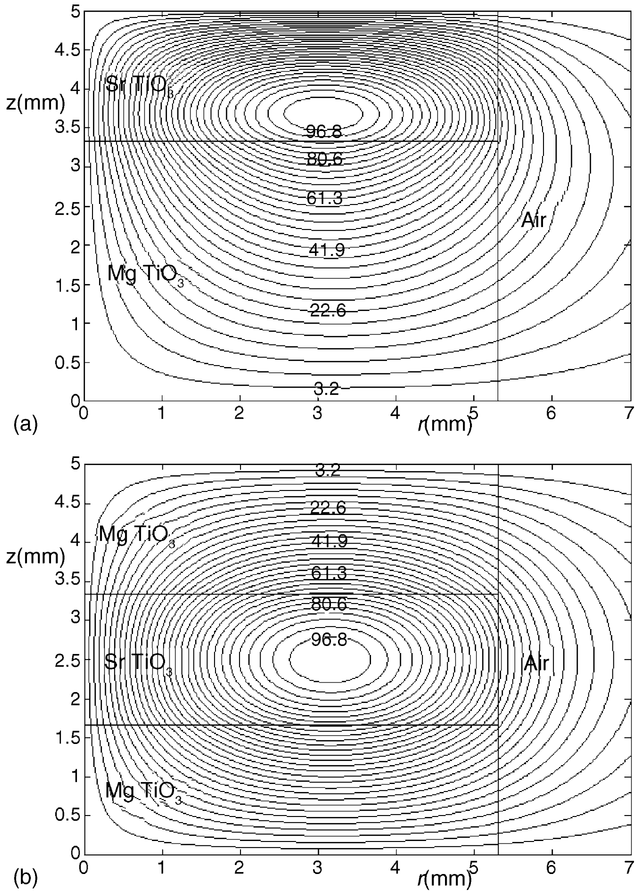

Fig. 5. Contours of the electric field intensity for the $MgTiO_3$–$SrTiO_3$ layered ceramics with the $SrTiO_3$ thickness fraction of 0.333, simulated by finite element method: (a) bi-layer $MgTiO_3$/$SrTiO_3$ ceramics; (b) tri-layer $MgTiO_3$/$SrTiO_3$/$MgTiO_3$ ceramics.

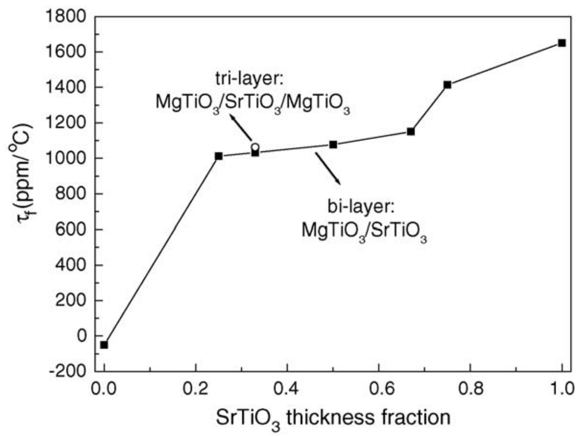

Fig. 6. Temperature coefficient of resonant frequency of the $MgTiO_3$–$SrTiO_3$ layered ceramics with TE_{011} mode.

Although the predicted resonant frequencies are lower and the effective dielectric constants are higher than the experimental results, the trends of the experimental and predicted curves are similar. The differences between the experimental and predicted results are due to the errors of the finite element analysis and the non-uniform diameters and inaccurate $MgTiO_3$–$SrTiO_3$ thickness ratios that can be hardly improved for the co-sintered layered ceramics. $SrTiO_3$ has much higher dielectric constant than $MgTiO_3$, so slight fluctuation of the dimensions may cause large variations of the resonant frequency and effective dielectric constant. Also, the relative error for the effective dielectric constant is much larger than that for the resonant frequency. This can be explained by Eq. (1), since the effective dielectric constant is proportional to the reciprocal square of the resonant frequency and the error of the resonant frequency is enlarged when calculating the effective dielectric constant.

For the constitutions of the layered ceramics reported by Cho et al., the dielectric constants of $Mg_{0.93}Ca_{0.07}TiO_3$ (MCT) and $(Ca_{0.3}Li_{0.14}Sm_{0.42})TiO_3$ (CLST) are 22.15 and 92.15, respectively.[10,11] It is assumed that the MCT–CLST layered ceramics have the same dimensions as those in the present work, since only the dimensions of the unsintered compacts have been reported (12 and 6 mm for the diameter and thickness, respectively).[16] Finite element method is also used to predict the resonant frequency and effective dielectric constant with TE_{011} mode for the reported bi- and tri-layer ceramics with the same CLST thickness fraction of 0.5, and the results are shown in Table 2. The predicted effective dielectric constant of the bi-layer ceramics fits the experimental value well, while large difference can be observed for the tri-layer ceramics, especially for the stacking arrangement of CLST/MCT/CLST. The reason is still unclear.

The temperature coefficient of resonant frequency as function of the $SrTiO_3$ thickness fraction is shown in Fig. 6. For the bi-layer ceramics, τ_f increases with increasing the $SrTiO_3$ thickness fraction. The tri-layer $MgTiO_3$/$SrTiO_3$/$MgTiO_3$ ceramics with the $SrTiO_3$ thickness fraction of 0.333 has higher τ_f than the bi-layer ceramics with the same thickness fraction. The result is consistent with that for the effective dielectric constant and it is also due to the different electric field distribution for the bi- and tri-layer ceramics, while the difference between the temperature coefficients of resonant frequency is much less than that between the effective dielec-

Table 2
Effective dielectric constant of the MCT–CLST layered ceramics with the same CLST thickness fraction of 0.5 (experimental after Refs. [10,11] and predicted by finite element method)

Configuration	MCT/CLST	MCT/CLST/MCT	CLST/MCT/CLST
Thickness ratio	1:1	0.5:1:0.5	0.5:1:0.5
$\varepsilon_{r,\mathrm{eff}}$ (after Refs. [10,11])	67.2	68.38	68.3
$\varepsilon_{r,\mathrm{eff}}$ (predicted)	64.59	80.35	38.32

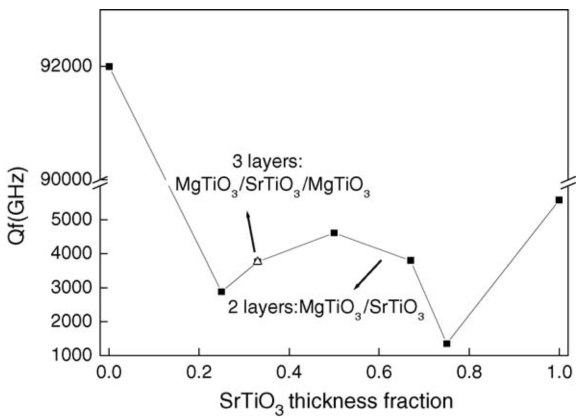

Fig. 7. Qf value of the $MgTiO_3$–$SrTiO_3$ layered ceramics with TE_{011} mode.

tric constants. This indicates that the effects of the stacking arrangement on the effective dielectric constant and temperature coefficient of resonant frequency are quite different. Further investigation on τ_f will be carried out to clarify the mechanism.

Fig. 7 shows the Qf value as function of the $SrTiO_3$ thickness fraction. The Qf value of the layered ceramics is significantly lower than those of $MgTiO_3$ and $SrTiO_3$, and the stacking arrangement seems to have little effect on it. The interface must play an important role, since if not, the Qf value of the layered ceramics shall be a combination of those of $MgTiO_3$ and $SrTiO_3$ and it shall be between them, just like the effective dielectric constant and temperature coefficient of resonant frequency. The different thermal expansion coefficients of $MgTiO_3$ and $SrTiO_3$ cause the residual stresses in the layered ceramics because of the $MgTiO_3$/$SrTiO_3$ interface, and the residual stresses shall be responsible for the different behavior of the Qf value.[9,10]

5. Conclusions

The microwave dielectric properties of $MgTiO_3$–$SrTiO_3$ layered ceramics with TE_{011} mode have been discussed in the present paper. With increasing $SrTiO_3$ thickness fraction, the resonant frequency decreases, while the effective dielectric constant and temperature coefficient of resonant frequency increase for the bi-layer ceramics. The stacking arrangement also has significant effect on the microwave dielectric properties of the layered ceramics. Moreover, finite element method gives a reliable explanation for the differences between the bi- and tri-layer ceramics. It is worthy to note that the temperature-stable layered $MgTiO_3$–$SrTiO_3$ ceramics can be attained by adjusting the $SrTiO_3$ thickness fraction. Also, more investigation on temperature coefficient of resonant frequency and Qf value shall be carried out in further work.

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