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# Microwave Dielectric Characteristics of $MgTiO_3/CaTiO_3$ Layered Ceramics

L. LI, X.M. CHEN & X.C. FAN
*Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China*

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**Abstract.** $MgTiO_3/CaTiO_3$ layered ceramics with differently stacking were fabricated and the microwave dielectric properties were evaluated with $TE_{011}$ mode. With increasing $CaTiO_3$ thickness fraction, the resonant frequency decreased and the dielectric constant increased with a near-linear relation for the bi-layer ceramics, while the values of the tri-layer $MgTiO_3/CaTiO_3/MgTiO_3$ ceramics with thickness ratio of 1:1:1 derived much from the curves of the bi-layer ceramics. The finite element method was used to give an explanation for the differences between the bi-layer and tri-layer ceramics.

**Keywords:** $MgTiO_3$, $CaTiO_3$, layered ceramics, microwave dielectric properties, finite element method

## 1. Introduction

Dielectric ceramics have been widely used for microwave applications and one of the basic requirements is near-zero temperature coefficient of resonant frequency [1–4]. However, the temperature stability of resonant frequency for many ceramics with high *Qf* value and high dielectric constant is not satisfactory and needs to be tuned [2–4]. Layered ceramics were introduced to improve the temperature stability as a new method by stacking one dielectric ceramic with positive temperature coefficient of resonant frequency and another ceramic with negative one, and near-zero temperature coefficient could be attained while maintaining the high *Qf* value [5–8]. On the other hand, impedance-stepped resonator as a new type of microwave resonator also promoted the research on layered ceramics [9–12]. However, the microwave dielectric behaviors and the mechanisms of the layered ceramics have not been investigated in detail and are to be further understood.

In the previous work, the dielectric properties of $MgTiO_3/CaTiO_3$ layered ceramics at 1 MHz have been measured by an LCR meter and the dielectric constant and temperature coefficient of dielectric constant of the layered ceramics fit the series rule well [13]. In the present work, the microwave dielectric properties of the $MgTiO_3/CaTiO_3$ layered ceramics with different stacking are evaluated with $TE_{011}$ mode and finite element method.

## 2. Experimental Details

$MgTiO_3$ and $CaTiO_3$ powders were synthesized by a solid state reaction process. MgO (97%), $CaCO_3$ (99%) and $TiO_2$ (99.5%) raw powders with the proper ratio were mixed by ball milling in distilled water with zirconia media for 24 hours and then calcined at $1100^oC$ in air for 3 hours to synthesize $MgTiO_3$ and $CaTiO_3$, respectively. $MgTiO_3$ and $CaTiO_3$ powders with organic binder of 5% PVA water solution were pressed into layered cylinders with various stacking and the individuals for compare. These compacts were sintered at 1350°C in air for 3 h and then taken to 1100°C with a small cooling rate of 1°C/min.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) observations were taken on the fractured surfaces. The resonant frequency and $Qf$ value at room temperature were determined by a network analyzer (Agilent 8720ES) with $TE_{011}$ mode using Hakki-Coleman method [14]. Assuming the layered ceramics as a homogeneous dielectric, the dielectric constant could be attained from the

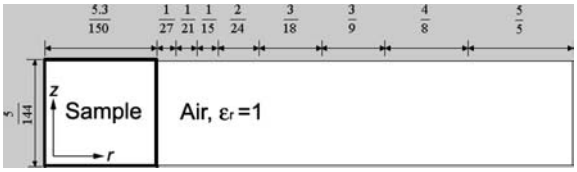


*Fig. 1.* Half of the cross section of the resonators for finite element analysis, where the fractional number $\frac{n}{m}$ denotes that the length is $n$ millimeters and divided into $m$ segments averagely.

resonant frequency and the dimensions of the layered ceramics by an accurate formula [14].

## 3. Finite Element Method

The axis symmetry exists for $TE_{011}$ mode and the electric field only has a rotational component $E_\theta$ that is also axis symmetrical, so 2-dimension 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, as shown in Fig. 1, since the electromagnetic energy concentrates in and around the sample and the space far from the sample can be neglected, and the triangular first-order element is employed for finite element analysis. More detailed analyzing process can be found in the previous papers [15, 16]. Finite element method can give the resonant frequencies corresponding to $TE_{0np}$ modes and the lowest one is the resonant frequency for $TE_{011}$ mode. The relative electric field intensity for each node is also given so that the contour of the electric field intensity can be plotted.

## 4. Results and Discussion

Different thermal expansion coefficients for $MgTiO_3$ and $CaTiO_3$ cause cracks for some layered ceramics. The bi-layer $MgTiO_3/CaTiO_3$ ceramics with thickness ratio of 1:1, 1:2 and 1:3 and tri-layer $MgTiO_3/CaTiO_3/MgTiO_3$ ceramics with thickness ratio of 1:1:1 can be successfully sintered without failure. The diameter and total thickness for all the ceramics are about 10.60 mm and 5.00 mm, respectively. The smooth $MgTiO_3/CaTiO_3$ interface with close bond can be observed in SEM photograph on the fractured surfaces, as shown in Fig. 2(a). Figure 2(b) and (c) are the

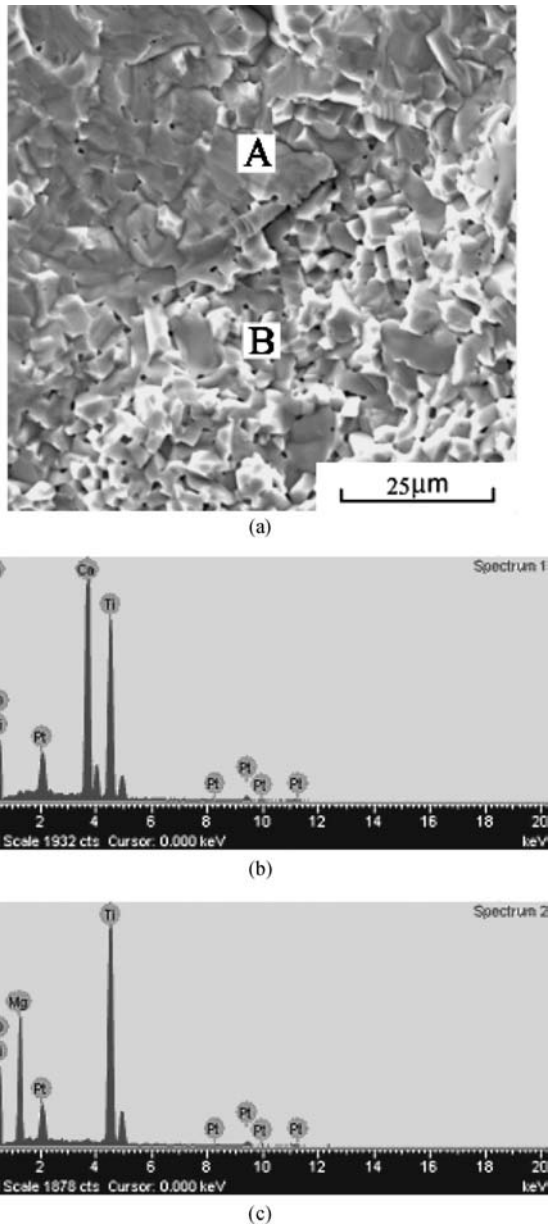


*Fig. 2.* (a) SEM photograph of fractured surfaces of $MgTiO_3/CaTiO_3$ layered ceramics (A: $CaTiO_3$; B: $MgTiO_3$); (b) EDS result of A area; c) EDS result of B area.

EDS results of the $CaTiO_3$ and $MgTiO_3$ areas near the interface and no distinct diffusion can be observed. The Pt peaks are introduced by the sputtered conducting Pt film for SEM observation.

Figures 3 and 4 show the resonant frequency and dielectric constant of layered $MgTiO_3/CaTiO_3$

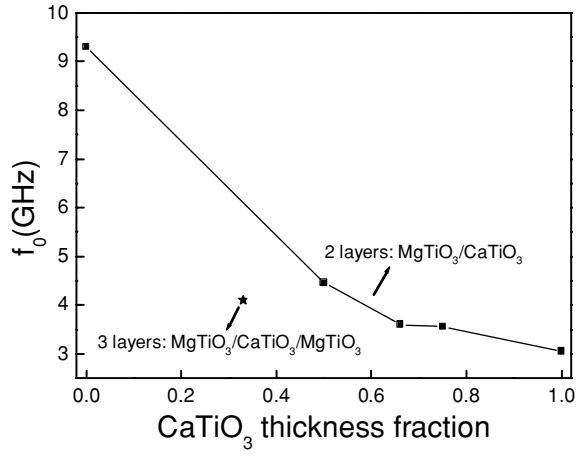


*Fig. 3*. Resonant frequency of the $MgTiO_3/CaTiO_3$ layered ceramics with $TE_{011}$ mode.

ceramics with $TE_{011}$ mode as function of $CaTiO_3$ thickness fraction. With increasing $CaTiO_3$ thickness fraction, the resonant frequency decreases and the dielectric constant increases with a near-linear relation for the bi-layer $MgTiO_3/CaTiO_3$ ceramics, while the tri-layer ceramics behaves much different from the bi-layer ceramics. The resonant frequency of tri-layer $MgTiO_3/CaTiO_3/MgTiO_3$ ceramics with thickness ratio of 1:1:1 is lower than the curve of the bi-layer $MgTiO_3/CaTiO_3$ ceramics, and the dielectric constant higher. The trend of the dielectric constant for bi-layer ceramics is very different from that at 1 MHz measured

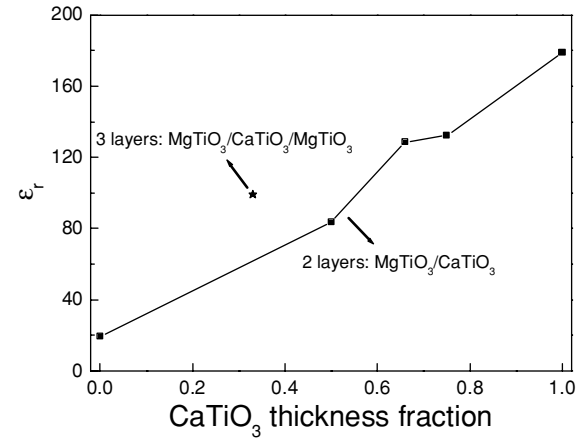


*Fig. 4*. Dielectric constant of the $MgTiO_3/CaTiO_3$ layered ceramics with $TE_{011}$ mode.

by an LCR meter, where the dielectric constant obeys the series rule very well [13]. Also, the dielectric constant at 1 MHz is determined by the net compositional ratio only and does not change significantly with the layer number [13]. The differences can be explained by the different electric field distributions. For the layered ceramics measured by an LCR meter, the electric field is perpendicular to the two electrode-plated paralleling surfaces and its intensity in a layer is uniform and inversely proportional to the dielectric constant of the layer [17]. But for the layered ceramics working as a dielectric resonator, the electric field distribution is much more complex. For the $TE_{011}$ mode in the present work, the electric field is rotational and its intensity is not uniform in a layer [18]. So the dielectric behaviors for the layered dielectric ceramics with $TE_{011}$ mode differ from those measured by an LCR meter, and it will be discussed detailedly in the following paragraphs.

The contour of the electric field intensity on half cross section of the layered ceramics is simulated by finite element method to explain the dielectric constant behavior of the layered ceramics with $TE_{011}$ mode. Figure 5(a) and (b) show the simulated contours with the relative electric field intensity marked for the bi-layer $MgTiO_3/CaTiO_3$ ceramics with thickness ratio of 2:1 and tri-layer $MgTiO_3/CaTiO_3/MgTiO_3$ ceramics with thickness ratio of 1:1:1. The $MgTiO_3/CaTiO_3$ net compositional ratios are all 2:1, but the electric field distributions are very different. The top and bottom paralleling metal plates are equivalent, and the electric field trends to concentrate in the area with large dielectric constant [18] (that is, $CaTiO_3$ layer), so the tri-layer $MgTiO_3/CaTiO_3/MgTiO_3$ ceramics with symmetric structure also has symmetric electric field distribution along thickness direction, while the $CaTiO_3$ layer of the asymmetric bi-layer ceramics seems to "pull" the contour of the electric field intensity towards the top side of the ceramics so that the bi-layer ceramics has asymmetric electric field distribution, as shown in Fig. 5(a) and (b). The marked relative electric field intensity shows that denser electric field distributes in $CaTiO_3$ layer for $MgTiO_3/CaTiO_3/MgTiO_3$ than for $MgTiO_3/CaTiO_3$. Also, electric filling factor ($P_e$) is introduced as a parameter to judge the contribution for each layer to the final microwave dielectric properties, which is defined by the ratio of the electric energy stored in a layer and the whole electric energy [18]. Electric filling factor can be easily calculated by the electric field intensity of each node and the dielectric constant for each layer, and

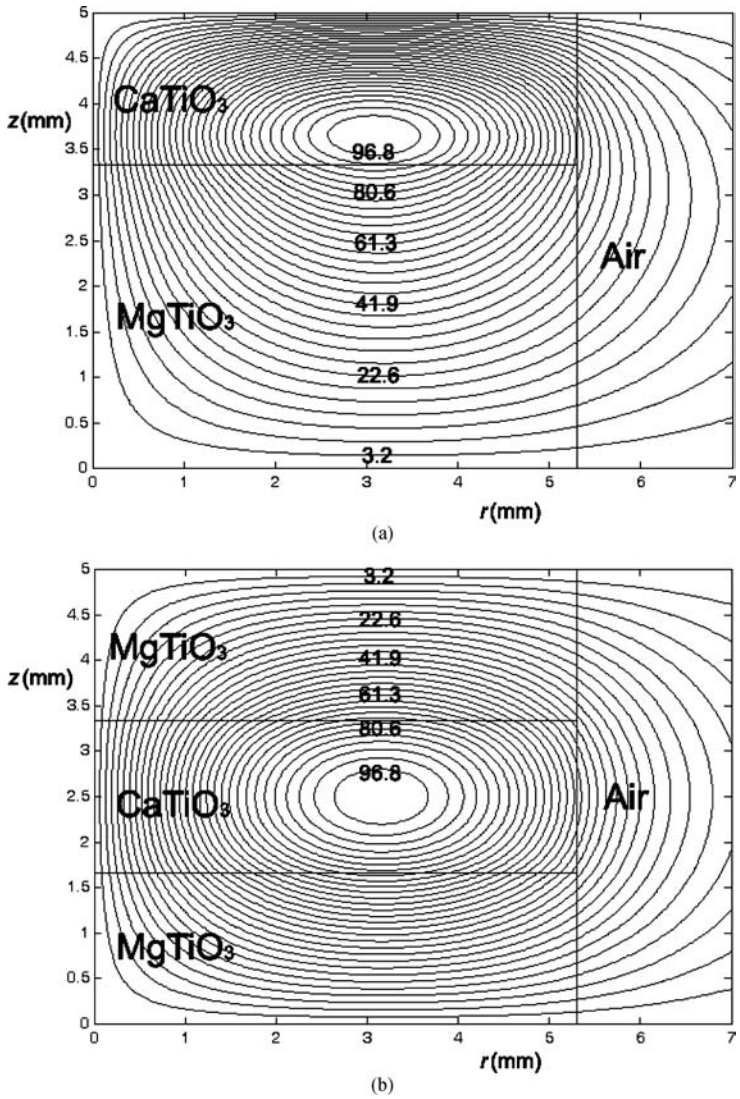


*Fig. 5.* Contours of the electric field intensity in the layered ceramics with $TE_{011}$ mode, simulated by finite element method: (a) bi-layer; (b) tri-layer.

the results are shown in Table 1. It is indicated that $P_e(CaTiO_3)$ for the tri-layer ceramics is larger than that for the bi-layer ceramics and $P_e(MgTiO_3)$ less. All these observations show that $CaTiO_3$ layer contributes more and $MgTiO_3$ contributes less to the final microwave dielectric properties for the tri-layer ceramics than for the bi-layer ceramics. Also, $CaTiO_3$ has much higher dielectric constant than $MgTiO_3$, so the resonant frequency is lower and dielectric constant higher for the tri-layer ceramics comparing with the bi-layer ceramics.

*Table 1.* Electric filling factor of $MgTiO_3$ and $CaTiO_3$ for the layered $MgTiO_3/CaTiO_3$ ceramics with the net thickness ratio of 2:1, predicted by finite element method.

| Stacking | Thickness ratio | $P_e(CaTiO_3)$ | $P_e(MgTiO_3)$ |
|---|---|---|---|
| $MgTiO_3/CaTiO_3$ | 2:1 | 0.924 | 0.075 |
| $MgTiO_3/CaTiO_3/MgTiO_3$ | 1:1:1 | 0.959 | 0.040 |

The predicted resonant frequencies and dielectric constants of the layered ceramics by finite element method are shown in Figs. 5–7. The trends of the experimental and predicted curves are similar, but the predicted resonant frequencies are lower and dielectric

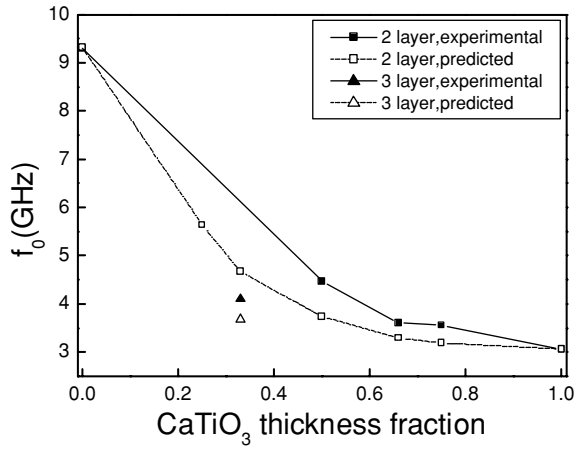


*Fig. 6.* Resonant frequency of the $MgTiO_3/CaTiO_3$ layered ceramics with $TE_{011}$ mode (experimental and predicted by finite element method).

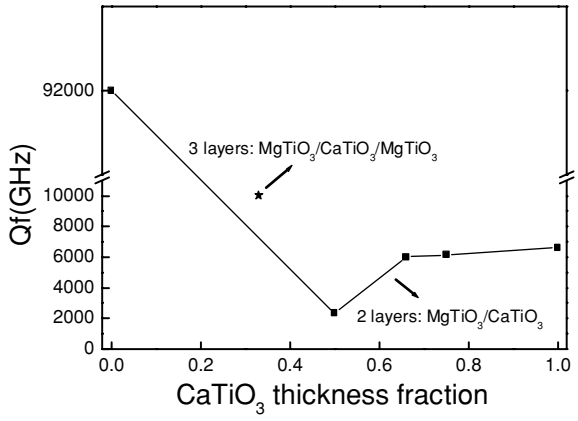


*Fig. 8.* $Qf$ value of the $MgTiO_3/CaTiO_3$ layered ceramics with $TE_{011}$ mode.

constants higher than the experimental results. The errors may be due to the nonuniform diameters and inaccurate $MgTiO_3/CaTiO_3$ thickness ratios that can be hardly improved for the co-sintered layered ceramics. $CaTiO_3$ has much higher dielectric constant than $MgTiO_3$, so slight fluctuation of the dimensions may cause large difference for the resonant frequency and dielectric constant.

Figure 8 shows the $Qf$ value of the layered ceramics as function of $CaTiO_3$ thickness fraction. The $Qf$ values of the layered ceramics are significantly lower than that of $MgTiO_3$. The different thermal expansion coefficients of $CaTiO_3$ and $MgTiO_3$ will bring stresses near the interfaces of the layered ceramics during the cooling process after sintering. The residual stresses [10, 11] and the low $Qf$ value of $CaTiO_3$ will lead to the lower $Qf$ value in the layered ceramics. Moreover, the $Qf$ value of the bi-layer ceramics decreases with decreasing the $CaTiO_3$ thickness fraction, and this can be interpreted in the following. The layered ceramics with lower $CaTiO_3$ thickness fraction will indicate the increased residual stress and subsequently the decreased $Qf$ value in the $CaTiO_3$ layer, and therefore the decreased $Qf$ value is observed for the layered ceramics.

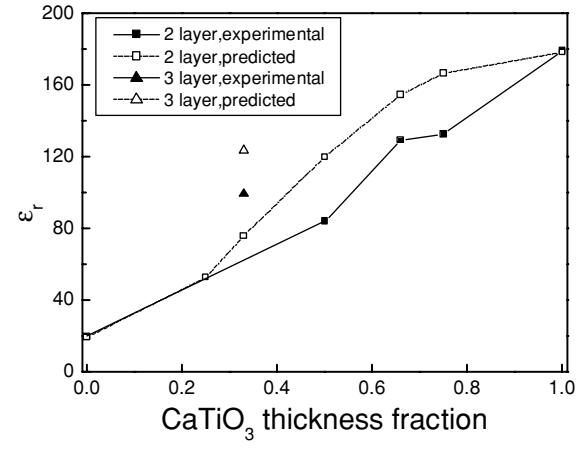


*Fig. 7.* Dielectric constant of the $MgTiO_3/CaTiO_3$ layered ceramics with $TE_{011}$ mode (experimental and predicted by finite element method).

## 5. Conclusion

$MgTiO_3/CaTiO_3$ layered ceramics with different stacking were fabricated and the microwave dielectric properties with $TE_{011}$ mode were evaluated. With increasing $CaTiO_3$ thickness fraction, the resonant frequency decreased and dielectric constant increased for the bi-layer ceramics, while the values of the tri-layer ceramics derived much from the curves of the bi-layer ceramics. The finite element method was used to predict the resonant frequency and indicated that the different electric field distributions should be responsible for the different behaviors between the bi-layer and tri-layer ceramics.

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## References

1. R. Freer, *Silic. Ind.*, **58**, 191 (1993).
2. W. Wersing, *Curr. Opin. Solid State Mater. Sci.*, **1**, 715 (1996).
3. M.P. Seabra, A.N. Salak, V.M. Ferreiraa, J.L. Ribeiro, and L.G. Vieira, *J. Euro. Ceram. Soc.*, **24**, 2995 (2004).
4. E.S. Kim and K.H. Yoon, *J. Euro. Ceram. Soc.*, **23**, 2397 (2003).
5. M.E. Tobar, J. Krupka, E.N. Ivanov, and R.A. Woode, *J. Phys. D: Appl. Phys.*, **30**, 2770 (1997).
6. J. Breeze, S.J. Penn, M. Poole, and N. McN. Alford, *Elect. Lett.*, **36**, 883 (2000).
7. M.E. Tobar, J.G. Hartnett, E.N. Ivanov, D. Cros, P. Blondy, and P. Guillon, *IEEE Trans. Microwave Theory Tech.*, **48**, 1265 (2000).
8. M.T. Sebastian, I.N. Jawahar, and P. Mohanan, *Mater. Sci. Eng.*, **B97**, 258 (2003).
9. M. Sagawa, M. Makimoto, and S. Yamashita, *IEEE Trans. Microwave Theory Tech.*, **45**, 1078 (1997).
10. J.Y. Cho, K.H. Yoon, and E.S. Kim, *Jpn. J. Appl. Phys.*, **41**, 4601 (2002).
11. J.Y. Cho, K.H. Yoon, and E.S. Kim, *Mater. Chem. Phys.*, **79**, 286 (2003).
12. J.Y. Cho, K.H. Yoon, and E.S. Kim, *J. Am. Ceram. Soc.*, **86**, 1330 (2003).
13. L. Li and X.M. Chen, *Mater. Sci. Eng.*, **B99**, 255 (2003).
14. B.W. Hakki and P.D. Coleman, *IEEE Trans. Microwave Theory Tech.,* **8,** 402(1960).
15. P.S. Kooi, M.S. Leong, and A.L.S. Prakash, *IEE Proc.*, **132**, 7 (1985).
16. Y.G. Zeng, G.H. Xu, and G.X. Song, *Electromagnetic Field Finite Element Method* (Science Press, Beijing, 1982).
17. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics* (2nd Edition) (John Wiley & Sons, New York, 1976).
18. D. Kajfez and P. Guillon, *Dielectric Resonators* (2nd edition), (Noble Publishing Corporation, Atlanta, 1998).