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New dielectric material system of $La(Mg_{1/2}Ti_{1/2})O_3$–$Ca_{0.6}La_{0.8/3}TiO_3$ for microwave applications

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The microstructure and microwave dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system with ZnO additions (0.5 wt.%) investigated by the conventional solid-state route have been studied. Doping with ZnO (0.5 wt.%) can effectively promote the densification and the dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 0.5 wt.% ZnO addition possess a dielectric constant (ε_r) of 43.6, a $Q\times f$ value of 48,000 (at 8 GHz) and a temperature coefficient of resonant frequency (τ_f) of −1 ppm/°C sintering at 1475 °C. As the content of $La(Mg_{1/2}Ti_{1/2})O_3$ increases, the highest $Q\times f$ value of 62,900 (GHz) for $x = 0.8$ is achieved at the sintering temperature 1475 °C. A parallel-coupled line band-pass filter is designed and simulated using the proposed dielectric to study its performance.

1. Introduction

Candidate materials for microwave dielectric resonators suitable for 3G technology must satisfy three main criteria: high quality factor ($Q > 15{,}000$), high dielectric constant (ε_r) > 25, and a near-zero temperature coefficient of resonant frequency ($\tau_f = \pm 3$ ppm/°C) [1,2]. Small temperature coefficients of the resonant frequency ensure the stability of the microwave components at different working temperatures. To satisfy the demands of microwave circuit designs, each dielectric property requires precise control. Using two or more compounds with negative and positive temperature coefficients to form a solid solution or mixed phases is the most promising method of obtaining a zero temperature coefficient of the resonant frequency, in our previous reports [1–3].

Although most dielectric ceramics with high dielectric constants have positive τ_f values, material with a high dielectric constant, high Q and negative τ_f are desired to achieve this goal. Seo-Yong Cho et al. have reported many complex perovskites $A(B^{2+}_{1/2}B^{4+}_{1/2})O_3$ with negative τ_f [4]. Among them, $La(Mg_{1/2}Ti_{1/2})O_3$ has a high dielectric constant ($\varepsilon \sim 29$), a high quality factor ($Q\times f$ value ~75,500 GHz) and a negative τ_f value (−65 ppm/°C). The crystal structure of $La(Mg_{1/2}Ti_{1/2})O_3$ was reported to be cubic. $Ca_{0.6}La_{0.8/3}TiO_3$ ($\varepsilon_r = 100$, $Q\times f = 20{,}000$ GHz, $\tau_f = 212$ ppm/°C) [5] with a positive τ_f value was introduced to into the mixture form a solid solution $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ to compensate for the τ_f value.

Many kinds of dielectric ceramics have been developed for microwave applications [6–8]. $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics have suitable dielectric constant and quality factors for application in dielectric resonators and filters [9]. However, pure $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics require a very high sintering temperature (1600 °C). There are three approaches to reducing the sintering temperature of microwave dielectric ceramics: low melting sintering aids addition [10–12], chemical processing, and the use of smaller particles as the starting materials. Of these three, sintering aids addition is the most effective and least expensive. However, no liquid phase sintering of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ with sintering aids addition has been reported yet. Previously, ZnO was researched and found to have good dielectric properties. In this paper, ZnO was used as a sintering aid for reducing the sintering temperature of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. The effects of ZnO on the sintering and microwave dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics were investigated.

A parallel-coupled line band-pass filter is designed and simulated using the proposed dielectric to study its performance (Table 1). This design approach enables one to use an EM simulator (IE3D) to complete the filter design in order to determine the physical dimensions of the filters.

2. Experimental procedures

Samples of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ were synthesized by conventional solid-state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of ZnO (0.5 wt.%) was added as a sintering aid. High purity oxide powders (>99.9%) La_2O_3, MgO, $CaCO_3$, TiO_2 and ZnO

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Table 1
Simulation results of the parallel-coupled line band-pass filter using different dielectrics.

Substrate	tan δ	ε_r	Size (mm^2)	Insertion loss (dB)	Return loss (dB)	f_o
FR4	0.015	4.5	82.26 × 10.77	3	17	2
Al_2O_3	0.0003	9.8	59.94 × 7.23	0.92	15	2
$0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$	0.00016	43.6	29.98 × 3.46	0.73	15	2

were weighed and mixed for 24 h with distilled water. The mixture was dried at 100 °C and thoroughly milled before it was calcined at 1200 °C for 4 h. The calcined powder was ground and sieved through 100-mesh screen. Phase formation of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ was confirmed using X-ray diffraction. The calcined powders were then re-milled for 24 h with PVA solution as a binder. Pellets with 11 mm in diameter and 5 mm in thickness were pressed using uniaxial pressing. A pressing pressure of 2000 kg/cm^2 was used for all samples. After debinding, these pellets were sintered at temperatures 1400–1500 °C for 5 h in air. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochrometer in the 2θ range of 20–60°. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL–40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki and Coleman [13] dielectric resonator method as modified and improved by Courtney [14]. The dielectric resonator was positioned between two brass plates. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 °C to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf),

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \qquad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. 3.Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 0.5 wt.% ZnO-doped $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics at different sintering temperatures (1400–1500 °C). All the peaks were indexed based on the cubic perovskite unit cell. The figure reveals that a series of extra peaks were present at the 1/2(1 1 1) ($2\theta = 19.56°$), 1/2(2 1 0) ($2\theta = 25.309°$), 1/2(3 0 0) ($2\theta = 34.5°$) and 1/2(3 1 1) ($2\theta = 37.98°$) positions. The X-ray diffraction patterns of the $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ solid solution have no significant change with 0.5 wt.% ZnO addition at sintering temperatures of 1400–1500 °C. Second phase was not observed at the level of 0.5 wt.% ZnO addition since that detection of a minor phase by X-ray is extremely difficult. Fig. 1 XRD patterns of $La(Mg_{1/2}Ti_{1/2})O_3–Ca_{0.6}La_{0.8/3}TiO_3$ ceramic systems form solid solution, and all peaks match with $La(Mg_1Ti_{1/2})O_3–Ca_{0.6}La_{0.8/3}TiO_3$ compound.

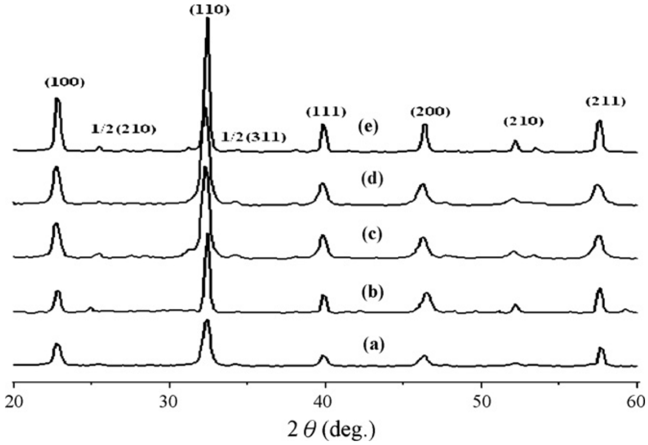

Fig. 1. X-ray diffraction patterns of $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 0.5 wt.% ZnO addition sintered at different temperatures for 5 h: (a) 1400 °C, (b) 1425 °C, (c) 1450 °C, (d) 1475 °C, and (e) 1500 °C.

The SEM photographs of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at 1450 °C for different x values are illustrated in Fig. 2. For all compositions, low level porosity and densed ceramic could be observed. The grain size was increased as increasing the $Ca_{0.6}La_{0.8/3}TiO_3$ content.

The SEM photographs of $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at various temperatures for 5 h are illustrated in Fig. 3. For all compositions, low level porosity and densed ceramic could be observed in the figure. The degree of the grain growth increased with the increase in sintering temperature. Porous specimens could not be observed for all sintered ceramics. It may play an important role to degrade the lattice vibration and get the high Q value. However, $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ inhomogeneous grain growth was observed at temperatures higher than 1475 °C with 0.5 wt.% ZnO additive, which might degrade the microwave dielectric properties of the ceramics. The inhomogeneous rod-like grains were identified, in all samples. It is possible to evaluate the effect of grain orientation on the XRD patterns as can be seen in Fig. 1 have lattice constant vibrational. At 1500 °C, the phenomenon of abnormal grain growth occurs in soap foams and polycrystalline ceramics for example. The driving force in these systems is the surface tension which leads to a reduction of the total surface area of the grains. Grain growth is the process that takes place during annealing of polycrystalline materials; its major feature is a systematic increase in grain size. Two different types of grain growth can be distinguished: the normal and abnormal grain growth. On the contrary, when the abnormal grain growth is the dominant mechanism, there are certain grains (abnormal grains) in the microstructure that grow much faster than the majority of the grains and in the end consume the fine-grained matrix around them. There has been a lot of work done in the field of abnormal grain growth, but the actual mechanism of abnormal grain formation and development from a uniform grain size distribution is not fully understood.

The density of the ZnO-doped $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics at differential sintering temperature as shown in Fig. 4. It indicated that densities of 4.575–5.29 g/cm^3 were obtained for ZnO-doped $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics at sintering temperatures from 1400 °C to 1500 °C. The density increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 3, and was also affected by the composition and decreased with increasing x value. It suggested that more $Ca_{0.6}La_{0.8/3}TiO_3$ contents and sintering at higher temperatures (above 1475 °C owing to the over-sintering) would degrade the bulk density of the ceramics.

The dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ with 0.5 wt.% ZnO addition are illustrated in Fig. 5. As the x value increased from 0.4 to 0.8, the dielectric constants decreased from 50.3 to 33.2. The dielectric constants slightly decreased with increasing sintering temperature. The decrease of ε_r value with increasing sintering temperature could be explained owing to the over-sintering of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)Ca_{0.6}La_{0.8/3}TiO_3$. With 0.5 wt.% ZnO addition, a ε_r value of 43.6 was obtained for $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at 1475 °C.

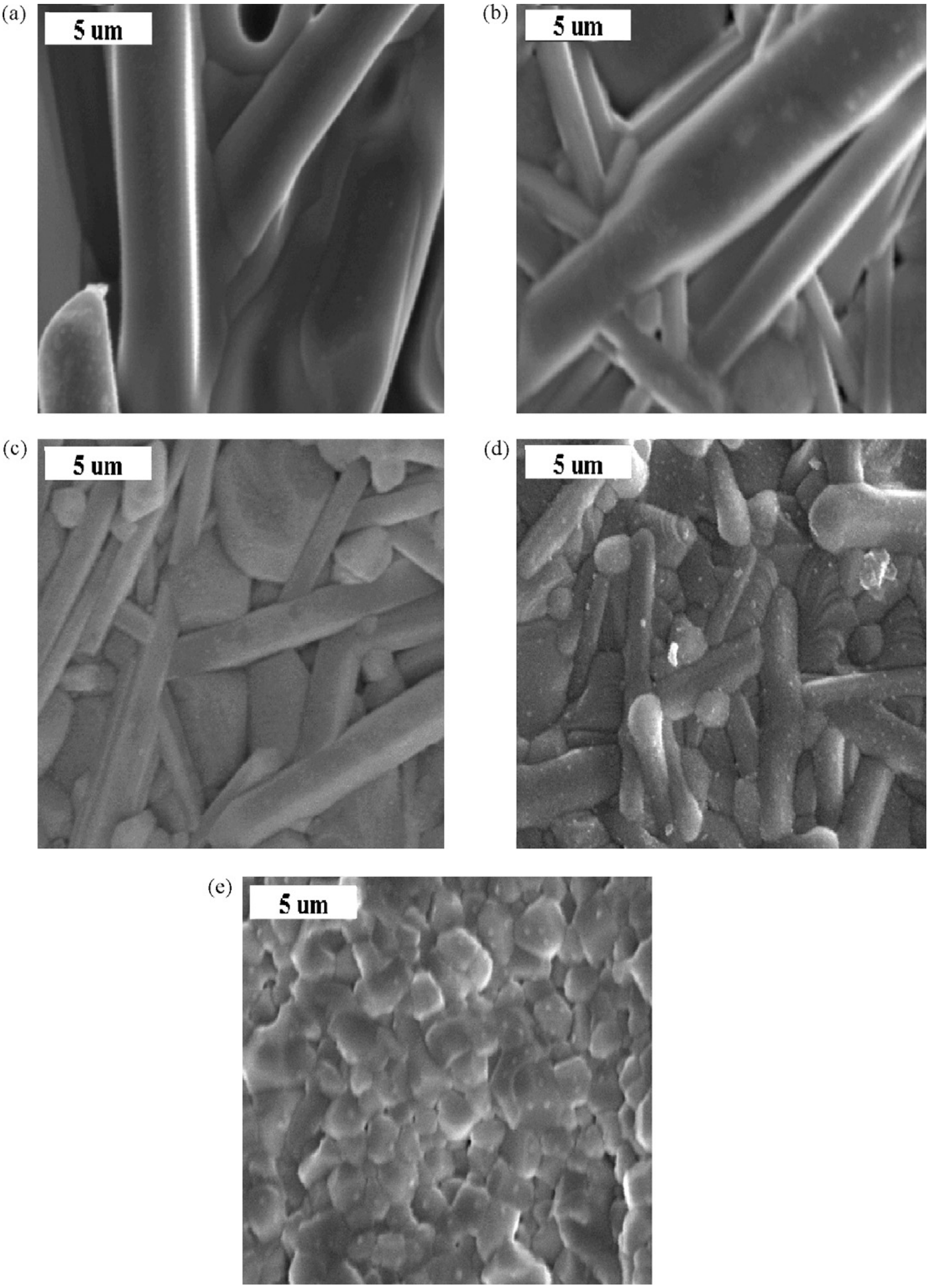

Fig. 2. SEM photographs of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)$ $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics: (a) $x = 0.4$, (b) $x = 0.5$, (c) $x = 0.6$, (d) $x = 0.7$ and (e) $x = 0.8$ with 0.5 wt.% ZnO additions sintered at 1450 °C for 5 h.

Fig. 6 shows the $Q \times f$ values of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics with 0.5 wt.% ZnO additions at different sintering temperatures as functions of the x value and with different x values had a maximum value at 1500 °C. The $Q \times f$ value increases with the increase in $\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ content and sintering temperature. It was expected since that the quality factor of $\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ is much higher than that of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ and the bulk density increased with increasing sintering temperature due to the ceramics being denser. Many factors could affect the microwave dielectric loss of dielectric resonators such as the lattice vibration modes, the pores and the secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and the dielectric loss was thus reduced. It seems that the dielectric loss of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics system was dominated by the bulk density and the grain size.

The temperature coefficients of resonant frequency (τ_f) of ZnO-doped $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)$ $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at

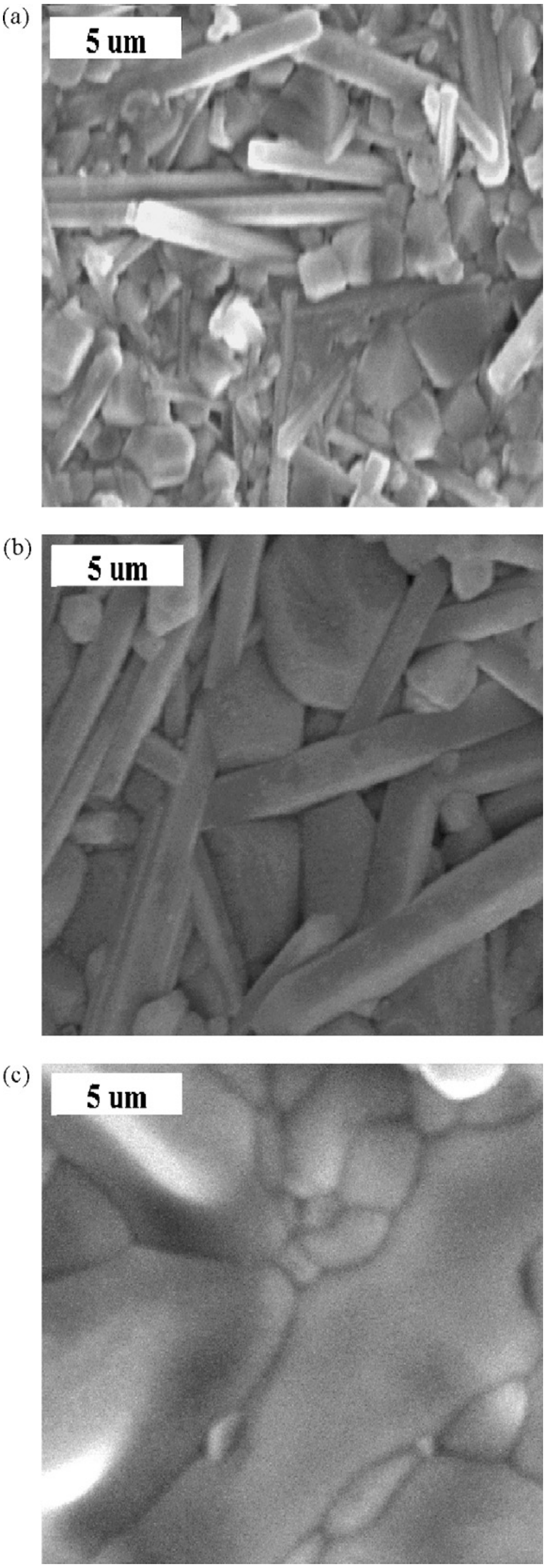

Fig. 3. SEM photographs of $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at: (a) 1400 °C, (b) 1450 °C and (c) 1500 °C with 0.5 wt.% ZnO additions for 5 h.

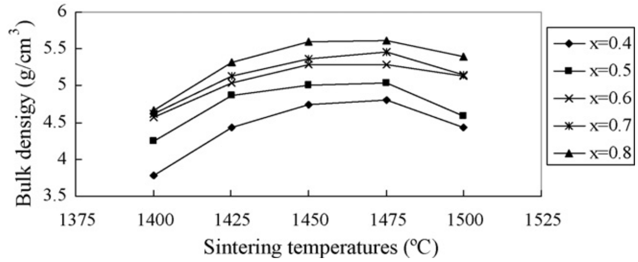

Fig. 4. Bulk density of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with 0.5 wt.% ZnO addition.

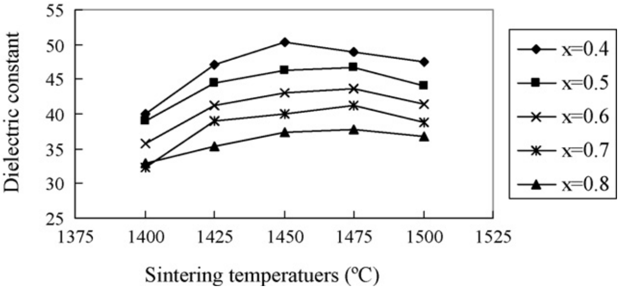

Fig. 5. ε_r value of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with 0.5 wt.% ZnO addition.

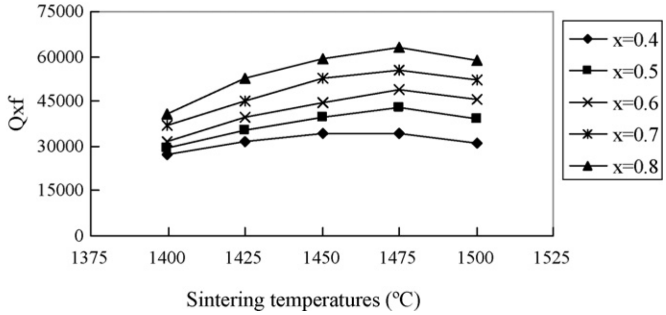

Fig. 6. $Q \times f$ value of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with various 0.5 wt.% ZnO additions.

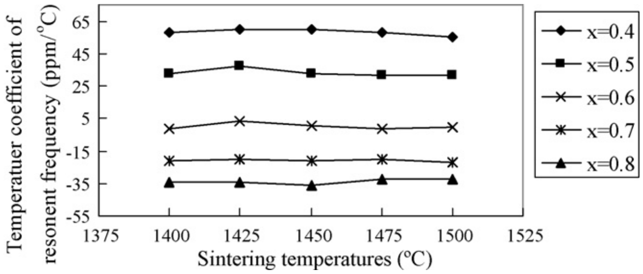

Fig. 7. Temperature coefficient value of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with 0.5 wt.% ZnO addition.

different sintering temperatures are illustrated in Fig. 7. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. It seemed that higher $Ca_{0.6}La_{0.8/3}TiO_3$ content would shift the τ_f value to more positive. It varied from −34 ppm/°C to 60 ppm/°C as the amount of $Ca_{0.6}La_{0.8/3}TiO_3$ addition increased from 0.4 to 0.8 sintered at 1475 °C. In general, the temperature coefficient of resonant frequency was found to be related to the composition and the existing phase in ceramics (Fig. 8).

Fig. 8. Physical layout of the parallel-coupled line band-pass filter.

4. Conclusion

The dielectric properties of ZnO-doped $x\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics were investigated. $x\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics exhibited perovskite structure. With 0.5 wt.% ZnO addition, a dielectric constant of 43.6, a $Q \times f$ value of 48,000 GHz and a τ_f value of -1 ppm/°C were obtained for $0.6\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$–$0.4\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics at 1475 °C for 4 h. The decrease in $Q \times f$ value at higher sintering temperature was owing to that the grain boundary phases were pronounced product. Therefore, the ZnO-doped $x\mathrm{La(Mg_{1/2}Ti_{1/2})O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramic is suitable for applications in microwave dielectric resonators and microwave device because of its excellent microwave dielectric properties.

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