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Letter

# High-dielectric-constant and low-loss microwave dielectric in the $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ solid solution system

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ABSTRACT

The microwave dielectric properties and microstructures of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics, prepared by a mixed oxide route, have been investigated. The forming of solid solutions was confirmed by the XRD patterns and the measured lattice parameters for all compositions. A near zero $\tau_f$ was achieved for samples with $x = 0.5$, although the dielectric properties varied with sintering temperature. The $Q \times f$ value of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5(Ca_{0.8}Sr_{0.2})TiO_3$ increased up to 1475 °C, after which it decreased. The decrease in dielectric properties was coincident with the onset of rapid grain growth. The optimum combination of microwave dielectric properties was achieved at 1475 °C for samples where $x = 0.5$ with a dielectric constant $\varepsilon_r$ of 47.12, a $Q \times f$ value of 35,000 GHz (measured at 6.2 GHz) and a $\tau_f$ value of −4.7 ppm/°C.



## 1. Introduction

The development of a microwave dielectric resonator for applications in communication systems such as cellular phones, wireless location networks (WLAN), direct broadcasting satellites (DBS) and global positioning systems (GPS) has progressed rapidly in the past decade [1–4]. These dielectric resonators must satisfy three main criteria: a high dielectric constant for miniaturization, a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) for better selectivity and a near-zero temperature coefficient of resonant frequency ($\tau_f$) for stable frequency stability [5,6]. However, high-dielectric-constant materials exhibit high dielectric loss (low $Q \times f$ value), whereas low-loss ceramics are usually accompanied by a low $\varepsilon_r$ value [7].

Several complex perovskite ceramics $A(B^{2+}_{1/2}B^{4+}_{1/2})O_3$ (where A = La, Nd, Sm; $B^{2+}$ = Mg, Zn, Co, Ni, Mn; $B^{4+}$ = Ti and Sn) have been reported due to their excellent microwave dielectric properties [1,8–12]. Among them, $La(Mg_{0.5}Ti_{0.5})O_3$ exhibits dielectric properties of high $\varepsilon_r \sim 29$ and the $Q \times f$ value ~75,500 GHz [13,14]. However, the $\tau_f$ value (~–65 ppm/°C) is too high for many its practical applications. With the aim of providing compensation for the temperature coefficient, $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5CaTiO_3$ material was developed to show a near zero $\tau_f$ value but it was found to decrease the $Q \times f$ value to 12,400–24,470 GHz [15,16]. The substitution of $CaTiO_3$ by $Ca_{0.8}Sm_{0.4/3}TiO_3$ had been reported to result in a higher $Q \times f$ value of 26,500 GHz [17]. Still, the $Q \times f$ needs to be promoted before putting it to a practical application as GPS antennas. A number of dielectrics were also used as a $\tau_f$ compensator for $La(Mg_{0.5}Ti_{0.5})O_3$ [18–20].

In this work, instead of $CaTiO_3$ or $Ca_{0.8}Sm_{0.4/3}TiO_3$, $Ca_{0.8}Sr_{0.2}TiO_3$ ceramics ($\varepsilon_r \sim 181$, $Q \times f \sim 8300$ GHz, $\tau_f \sim 991$ ppm/° C [21]) was chosen as a compensator for $\tau_f$. The studied system turned out to show a much better combination of microwave dielectric properties. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction (XRD) patterns and the microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

## 2. Experimental procedure

Samples of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ($x = 0.2$–$0.8$) were synthesized by the conventional solid-state method. The starting materials were high-purity oxide powders (>99.9%): $CaCO_3$, $SrCO_3$, $La_2O_3$, MgO and $TiO_2$. Stoichiometric mixtures of $(Ca_{0.8}Sr_{0.2})TiO_3$ and $La(Mg_{0.5}Ti_{0.5})O_3$ were separately prepared and ground in distilled water for 24 h in a ball mill using agate balls. $(Ca_{0.8}Sr_{0.2})TiO_3$ and $La(Mg_{0.5}Ti_{0.5})O_3$ powders were calcined at 1100 °C and 1200 °C for 4 h, respectively. The calcined powders were mixed according to the molar fraction $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ and re-milled for 24 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder (PVA 500, Showa, Japan) was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. These pellets were sintered at temperatures of 1375–1525 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The bulk X-ray diffraction (XRD, Siemens D5000) spectra were collected using Cu $K\alpha$ ($\lambda = 0.15406$ nm) radiation (at 40 kV and 40 mA) and a graphite monochrometer in the $2\theta$ range of 20–60°. The microstructures were evaluated surfaces by scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, the Netherlands).

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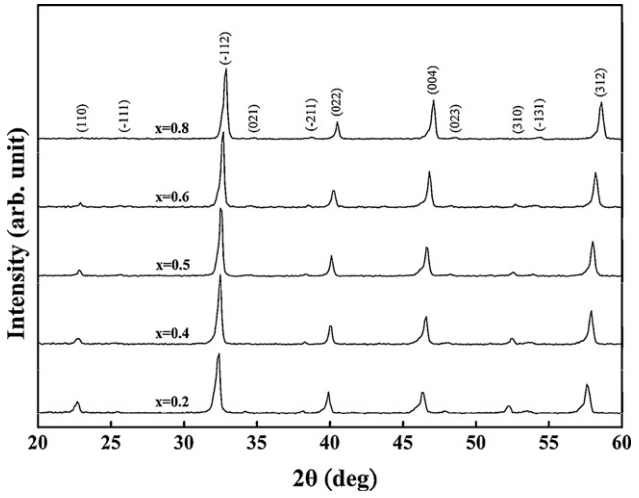


**Fig. 1.** X-ray diffraction patterns of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1475 °C for 4 h with different $x$ values.

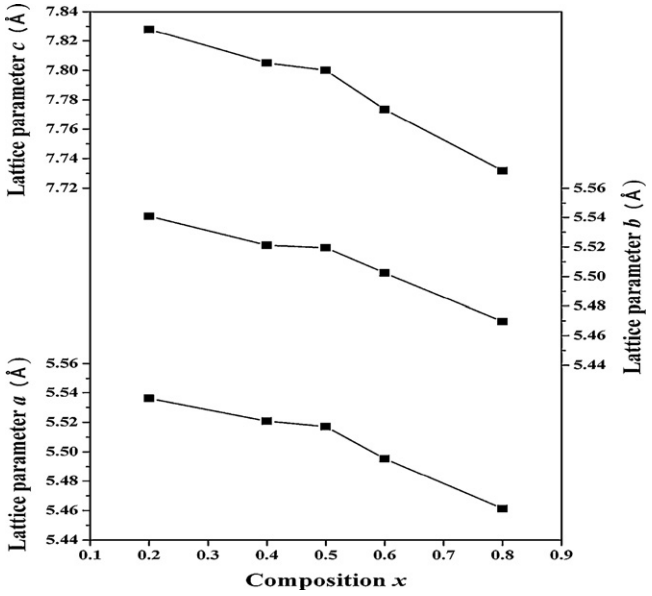


**Fig. 2.** The lattice parameters of the $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ solid solutions.

The apparent densities of the sintered pellets were measured by the Archimedes method. The dielectric constant ($\varepsilon_r$) and the quality factor values ($Q$) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [22,23]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. For temperature coefficient of resonant frequency ($\tau_f$), the technique is the same as that of quality factor measurement. The test set was placed over a thermostat in the temperature range of +25 to +80 °C. $\tau_f$ (ppm/°C) can be calculated by considering the change in resonant frequency ($\Delta f$).

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

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

## 3. Results and discussion

Fig. 1 shows the room temperature XRD patterns recorded for $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system at 1475 °C for 4 h. The complex-perovskite structure (Monoclinic: ICDD-PDF #01-072-6152) was identified without any second phase for all compositions tested in the experiment. As the $x$ value increases, the peaks in the XRD spectra shift to a higher angle implying the forming of solid solution. This is because the ionic radius of $La^{3+}$ (1.032 Å) in $La(Mg_{0.5}Ti_{0.5})O_3$ and $0.8Ca^{2+} + 0.2Sr^{2+}$ (Ca = 1.00 Å, Sr = 1.18 Å) in $(Ca_{0.8}Sr_{0.2})TiO_3$ are similar; whereas $Mg^{2+}$ (0.72 Å) in $La(Mg_{0.5}Ti_{0.5})O_3$ is larger than that of $Ti^{4+}$ (0.605 Å) in $(Ca_{0.8}Sr_{0.2})TiO_3$ [24]. Although the superlattice peak is barely detectable, it is almost certain that the entire solid solution is distorted due to rotation of the octahedral. This in itself will generate the superlattice at the (−1 1 1), (0 2 1) and (−2 1 1) positions. These positions are weak and may not be observable in XRD since X-ray is insensitive to small displacements. The measured lattice parameters (Fig. 2) almost linearly decrease from $x = 0.2$ to $x = 0.8$ further confirming it tends to form a continuous solid solution.

**Table 1**
Microwave dielectric properties of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1475 °C for 4 h.

| $x$ value | Apparent density (g/cm$^3$) | $\varepsilon_r$ | $Q \times f$ (GHz) | $\tau_f$ (ppm/°C) |
|---|---|---|---|---|
| 0.8 | 4.46 | 84.73 | 8,500 | 197 |
| 0.6 | 4.83 | 54.47 | 19,600 | 26.2 |
| 0.5 | 5.08 | 47.12 | 35,000 | −4.7 |
| 0.4 | 5.22 | 41.43 | 40,800 | −32.3 |
| 0.2 | 5.51 | 34.22 | 52,200 | −56.6 |

Table 1 demonstrates the microwave dielectric properties of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1475 °C for 4 h. The dielectric properties are functions of $x$ value. Notice that the ceramic system shows a good temperature stability ($\tau_f = -4.7$ ppm/° C) at $x = 0.5$ indicating a suitable composition for practical applications.

Fig. 3 shows the SEM photographs of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5(Ca_{0.8}Sr_{0.2})TiO_3$ (hereafter referred to as 5LMCST) ceramics after sintering at different temperatures for 4 h. Porous microstructures were observed at 1375 °C. The grain size increases as the sintering temperature increases and a noticeable grain growth and a relatively uniform surface morphology are observed at 1475 °C. Further increase in the sintering temperature would lead to a rapid grain growth resulting in a forming of pores as illustrated in Fig. 3(g).

Fig. 4 shows the apparent densities and $\varepsilon_r$ of 5LMCST ceramics after sintering at different temperatures for 4 h. With increasing sintering temperature, the apparent density increased to a maximum value of 5.08 g/cm$^3$ at 1475 °C and thereafter it slightly decreased. The increase of density was a result from grain growth, whereas the decrease of density was due to the presence of pores resulted from the rapid grain growth as shown in Fig. 3. Variation of $\varepsilon_r$ was consistent with that of density. The dielectric constant increased with increasing sintering temperature due to a denser specimen. After reaching its maximum at 1475 °C it decreased and a maximum $\varepsilon_r$ value of 47.12 can be achieved.

The $Q \times f$ and $\tau_f$ values of 5LMCST ceramics at different sintering temperatures for 4 h are demonstrated in Fig. 5. By increasing the sintering temperature, the $Q \times f$ value increased to a maximum value of 35,000 GHz (at 6.2 GHz) and thereafter it decreased. It showed a similar trend with that of density suggesting that the variation of $Q \times f$ was mainly a result from its corresponding density. In addition, uniform morphology also assisted in reducing the lattice imperfection and lowering the dielectric loss. Significant change in the temperature coefficient of resonant frequency ($\tau_f$) was not observed as expected because the $\tau_f$ value is mainly related to the compositional variance, the additives, and the existence of second phase of the material. A $\tau_f$ value of −4.7 ppm/°C is obtained for specimen sintered at 1475 °C for 4 h.

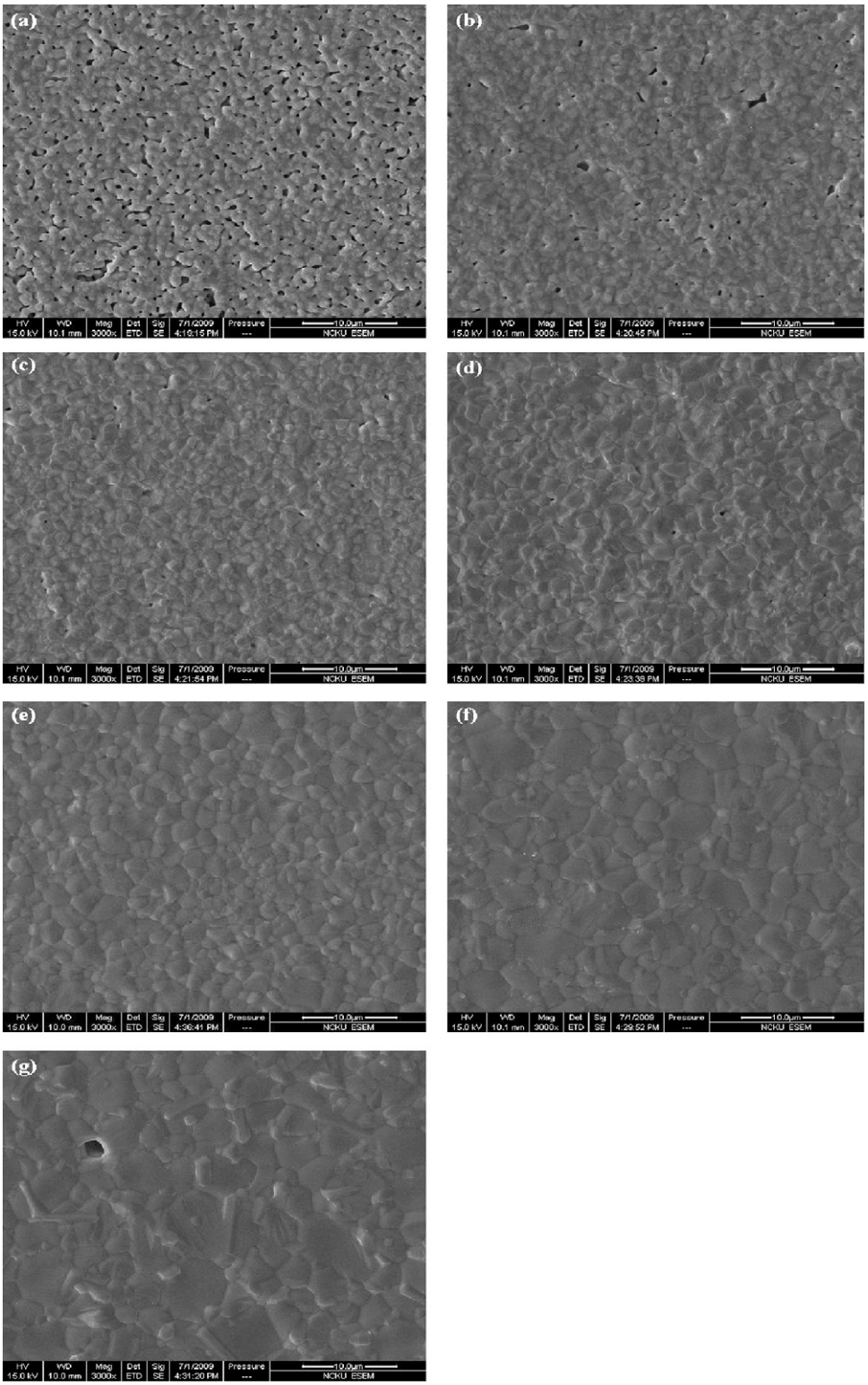


**Fig. 3.** SEM photographs of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics sintered at (a) 1375, (b) 1400, (c) 1425, (d) 1450, (e) 1475, (f) 1500 and (g) 1525 °C for 4 h.

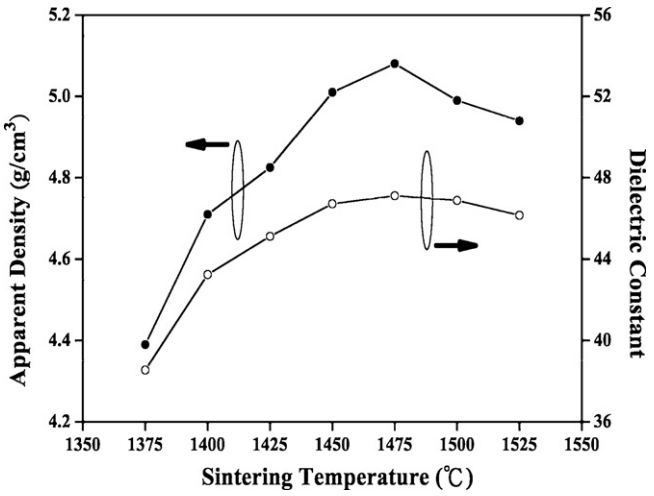


**Fig. 4.** Apparent density and dielectric constant of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics as a function of the sintering temperature.

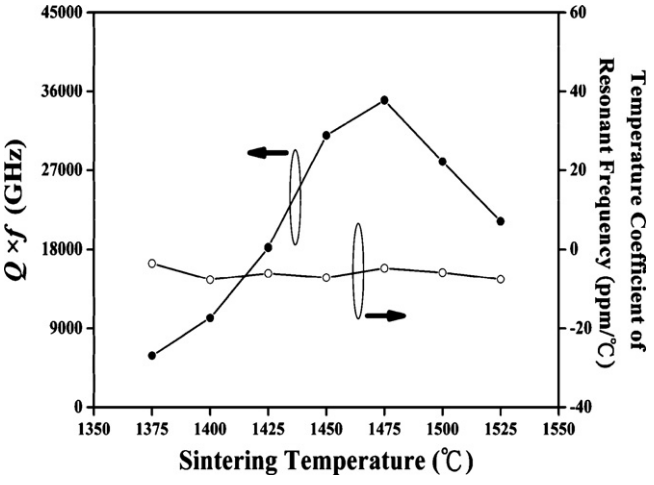


**Fig. 5.** $Q \times f$ and $\tau_f$ value of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics as a function of the sintering temperature.

## 4. Conclusion

The microwave dielectric properties and microstructures of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ have been investigated and the result show that these materials possess relatively high $Q \times f$, high dielectric constant and tunable $\tau_f$. The microwave dielectric properties are strongly correlated to the density and the compositional ratio of the specimen. The proposed system exhibits a good combination of $\varepsilon_r = 47.12$, $Q \times f = 35{,}000$ GHz, $\tau_f = -4.7$ ppm/° C, at $x = 0.5$, which can be as a suitable candidate material for today's 3G passive components particularly the small-sized GPS patch antennas.

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