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Effect of Bi_2O_3 additives on sintering and microwave dielectric behavior of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics

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Abstract

Bi_2O_3 was selected as liquid phase sintering aid to lower the sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics. The sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics is generally high, about 1600 °C. However, the sintering temperature was significantly lowered about 275 °C from 1600 °C to 1325 °C by incorporating in 15 mol% Bi_2O_3 and revealed the optimum microwave dielectric properties of dielectric constant (ε_r) value of 40.1, a quality factor ($Q \times f$) value of 60,231 GHz, and the temperature coefficient (τ_f) value of 70.1 ppm/°C. During all addition ranges, the relative dielectric constants (ε_r) were different and ranged from 32.0 to 41.9, the quality factors ($Q \times f$) were distributed in the range of 928–60,231 GHz, and the temperature coefficient (τ_f) varies from 0.3 ppm/°C to 70.3 ppm/°C. Noticeably, a nearly zero τ_f can be found for doping 5 mol% Bi_2O_3 sintering at 1325 °C. It implies that nearly zero τ_f can be achieved by appropriately adjusting the amount of Bi_2O_3 additions and sintering temperature for $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics.
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1. Introduction

The development of a microwave dielectric resonator for applications in communication system such as direct broadcasting satellite (DBS), global positioning systems (GPS), wireless location area networks (WLAN), as well as wireless mobile systems, has progressed rapidly in the past decade [1,2]. The unique electrical properties of ceramic dielectric resonators have revolutionized the microwave-based wireless communications industry by reducing the size and cost of filters in circuit systems. To miniaturize the devices and to work with high efficiency and stability for the systems, the materials for microwave resonators and microwave device substrates have to combine with a high dielectric constant ($\varepsilon_r > 25$), a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$), and a near-zero temperature coefficient of resonant frequency (τ_f). However, it is difficult to find the material that satisfied with above-mentioned three required characteristics [3,4].

Recently, $Ln(Mg_{0.5}Ti_{0.5})O_3$ (Ln = La, Sm, Nd, Dy, Y) ceramics have been reported [5–7] with low loss dielectric material and are suitable for microwave substrate applications. Among these perovskite compounds, $La(Mg_{0.5}Ti_{0.5})O_3$ (LMT) exhibited the relative low dielectric loss. Although LMT has a relative high dielectric constant ($\varepsilon_r > 25$) and quality factor (Q), it has a high negative temperature coefficient of resonant frequency (τ_f) of −65 ppm/°C and high sintering temperature of 1650 °C. Therefore, the objective of this paper is to develop a LMT dielectric material with lower sintering temperature, high dielectric constant, high quality factor and nearly zero τ_f and study the variation of microwave dielectric properties. Low temperature solid-state synthesis is an approach that shows great promise for the synthesis of materials. Usually, three methods are commonly used for reducing the sintering temperature of dielectric ceramics: low melting-temperature glass addition, chemical processing, and powder with smaller particle sizes [11–13]. The first method using liquid phase glass sintering was found to effectively lower the firing temperature. However, it also decreased the microwave dielectric properties of dielectric resonators, especially quality factor. The chemical process often required a flexible

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procedure, which was expensive and time consuming. Therefore, the selection of nonglass addition with low melting point is extremely important. Since Bi_2O_3 is commonly used as a liquid-phase flux and has been shown to accomplish a substantial sintering temperature reduction, it was selected as a sintering aid in the present study.

2. Experimental procedure

Specimen powders were prepared by a conventional solid-state method. High-purity oxide powders (>99.9%): La_2O_3, MgO and TiO_2 were used as raw materials. The powders were weighed according to the composition $La(Mg_{0.5}Ti_{0.5})O_3$, and were ground in distilled water for 12 h in a ball mill with agate balls. The prepared powders were dried, passed through a 200-mesh sieve and calcined at 1100 °C for 2 h in air. The calcined powers were mixed as desired composition $La(Mg_{0.5}Ti_{0.5})O_3$ with 5 mol%, 10 mol%, and 15 mol% of Bi_2O_3 sintering aids and re-milled for 12 h. These fine powders were mixed with 3 wt% organic binder (PVA) and pressed at 1000 kgf/cm^2 into pellets with dimensions of 11 mm diameter and 5 mm thickness. These pellets were sintered at temperatures of 1275–1375 °C for 6 h in air. The heating and cooling rates were both set at 5 °C/min.

The microstructure observation of the sintered ceramics surface was performed by means of scanning electron microscopy (SEM, JEOL JSM 6400, Japan). In order to define clearly the grain size, we use the lineal intercept technique to determine the grain size [14]. The average grain size, G_a, was calculated using the following relation: $G_a = 1.5 \cdot L/M \cdot N$, where 1.5 is a geometry-dependent proportionality constant [15], L is the total test line length, M is the magnification, and N is the total number of intercepts. The crystalline phase of sintered ceramics was identified by X-ray diffraction (XRD, RIGAKU D/Max-II) with Cu Kα radiation (λ = 1.5418 Å at 40 kV and 30 mA) and scanned from 20° to 80° with scanning speed of 4°/min. The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values ($Q \times f$) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method which had been modified and improved by Courtney [8,9]. The dielectric resonator was positioned between two brass plates. Microwave dielectric properties of sintered samples were measured by an Anritsu 37347C Network Analyzer. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity was placed over a thermostat in the temperature range of 30–80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (f), and is defined by:

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

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 XRD patterns of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics incorporated with (a) 5 mol% Bi_2O_3, (b) 10 mol% Bi_2O_3, and (c) 15 mol% Bi_2O_3 sintering aids sintered at different temperatures 1275 °C, 1300 °C, 1325 °C, 1350 °C and 1375 °C, respectively, for 6 h. Identical XRD patterns of Fig. 1(a)–(c) were observed and did not change significantly with different sintering temperatures in the range of 1275–1375 °C. No secondary phases for incorporating with various amount of Bi_2O_3 are observed since detection of a minor phase by X-ray is extremely difficult. In order to perform an extensive investigation on the structure and the formation of a solid solution, lattice parameters of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics incorporated with various amount of Bi_2O_3 sintering aids

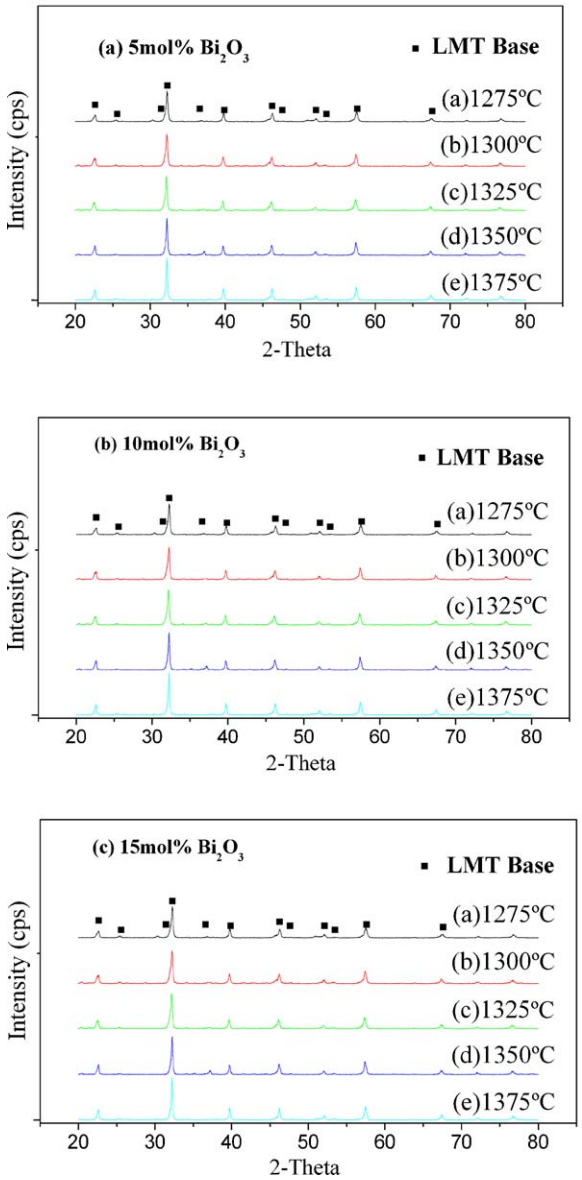

Fig. 1. XRD patterns of $La(Mg_{0.5}Ti_{0.5})O_3$ sintered at various temperatures for 6 h with (a) 5 mol%, (b) 10 mol%, and (c) 15 mol% Bi_2O_3 additives.

Table 1
Lattice parameters, cell volumes, crystal symmetries of $La(Mg_{0.5}Ti_{0.5})O_3$ (LMT) ceramics incorporated with 5 mol% Bi_2O_3 sintering aid sintered at various temperatures for 6 h.

Sintering temperature (°C)	Lattice parameter (Å)	Cell volume (Å^3)	Crystal symmetries
1275	$a = 5.617(2)$, $b = 7.835(3)$, $c = 5.549(2)$	244.21	Orthorhombic
1300	$a = 5.616(3)$, $b = 7.837(4)$, $c = 5.553(3)$	244.40	Orthorhombic
1325	$a = 5.532(3)$, $b = 7.869(2)$, $c = 5.560(4)$	242.03	Orthorhombic
1350	$a = 5.541(2)$, $b = 7.854(3)$, $c = 5.549(3)$	241.49	Orthorhombic
1375	$a = 5.541(2)$, $b = 7.852(3)$, $c = 5.550(3)$	241.47	Orthorhombic

Table 2
Lattice parameters, cell volumes, crystal symmetries of $La(Mg_{0.5}Ti_{0.5})O_3$ (LMT) ceramics incorporated with 10 mol% Bi_2O_3 sintering aid sintered at various temperatures for 6 h.

Sintering temperature (°C)	Lattice parameter (Å)	Cell volume (Å^3)	Crystal symmetries
1275	$a = 5.542(2)$, $b = 7.835(3)$, $c = 5.549(2)$	240.95	Orthorhombic
1300	$a = 5.549(3)$, $b = 7.835(4)$, $c = 5.552(3)$	241.38	Orthorhombic
1325	$a = 5.544(3)$, $b = 7.869(2)$, $c = 5.562(4)$	242.65	Orthorhombic
1350	$a = 5.524(2)$, $b = 7.856(3)$, $c = 5.549(3)$	240.81	Orthorhombic
1375	$a = 5.541(2)$, $b = 7.856(3)$, $c = 5.552(3)$	241.68	Orthorhombic

Table 3
Lattice parameters, cell volumes, crystal symmetries of $La(Mg_{0.5}Ti_{0.5})O_3$ (LMT) ceramics incorporated with 15 mol% Bi_2O_3 sintering aid sintered at various temperatures for 6 h.

Sintering temperature (°C)	Lattice parameter (Å)	Cell volume (Å^3)	Crystal symmetries
1275	$a = 5.596(2)$, $b = 7.835(3)$, $c = 5.549(2)$	243.29	Orthorhombic
1300	$a = 5.594(3)$, $b = 7.836(4)$, $c = 5.541(3)$	242.88	Orthorhombic
1325	$a = 5.545(3)$, $b = 7.869(2)$, $c = 5.561(4)$	242.64	Orthorhombic
1350	$a = 5.541(2)$, $b = 7.856(3)$, $c = 5.549(3)$	241.55	Orthorhombic
1375	$a = 5.542(2)$, $b = 7.856(3)$, $c = 5.541(3)$	241.24	Orthorhombic

and sintered at different temperatures are demonstrated in Tables 1–3.

The SEM images of polished and thermally etched surface from the specimens of $La(Mg_{0.5}Ti_{0.5})O_3$ incorporated with various amount of Bi_2O_3 sintering aids and sintering at different temperatures are illustrated in Figs. 2–4. As shown in Fig. 2, the 5 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with sintering temperatures of 1325–1375 °C revealed that the grain size of the ceramics increased notably with the increase in sintering temperature. The grain sizes are ranged from 3.74 μm to 7.22 μm which estimated by lineal intercept technique. There are some pores that are located at the grain boundaries or at the triple point. However, abnormal grain growth was observed at sintering temperatures of 1375 °C which might lead to degradation in the microwave dielectric properties of the ceramics. Abnormal growth occurs when a few large grains grow faster than the surrounding fine grained matrix. There are several reasons to invoke abnormal growth such as non-uniformities in impurity content, liquid phases or porosity that could induce local variation in growth rate. Fig. 3 shows the SEM micrographs of 10 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with sintering temperatures of 1325–1375 °C that revealed the grain growth remarkably at temperatures of 1375 °C. The average grain size is increased from 3.57 μm sintered at 1325 °C to 20.08 μm sintered at 1375 °C. This is ascribed to the formation of liquid phase, which accelerated the rate of grain growth. The SEM micrographs of 15 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with sintering temperatures of 1325–1375 °C are illustrated in Fig. 4. As the increase in sintering temperature, the grain size increased gradually from 3.83 μm sintered at 1325 °C to 4.95 μm sintered at 1375 °C. However, inhomogeneous grain growth was observed at temperature higher than 1350 °C, which might degrade the microwave dielectric properties of the ceramics.

Fig. 5 shows the bulk density of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various amount of Bi_2O_3 sintering aids as function of sintering temperatures. In all specimens, the densities increased with increasing sintering temperature due to the decrease in the number of pores as observed in SEM. Moreover, increasing the sintering temperature would enhance the grain growth resulting in an increase in the density. A maximum density of 5.5 g/cm^3 was obtained for 15 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ sintered at 1375 °C for 6 h. It implied that the microwave dielectric properties, grain sizes, grain morphology, and bulk density were greatly dependent on sintering temperature and sintering aids.

There are a number of factors that affect the microwave dielectric loss which can be divided into two kinds, the intrinsic

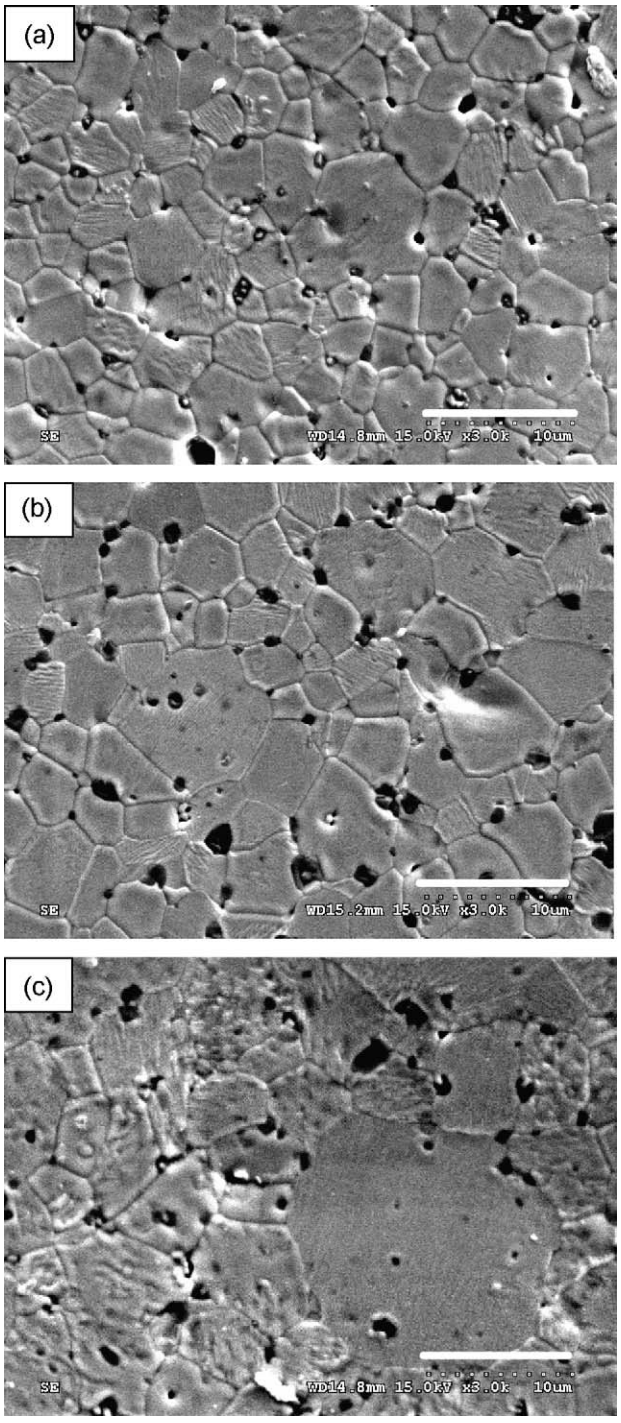

Fig. 2. SEM micrographs of 5 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at different temperatures: (a) 1325 °C, (b) 1350 °C, and (c) 1375 °C.

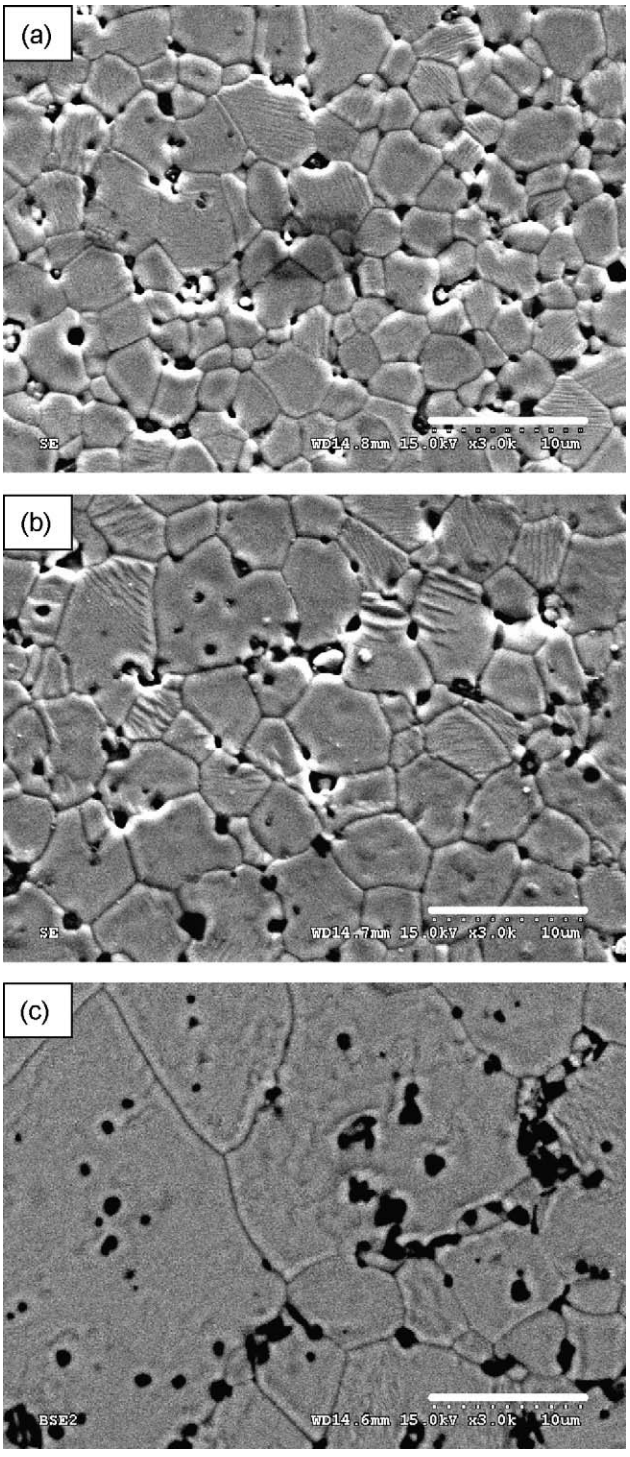

Fig. 3. SEM micrographs of 10 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at different temperatures: (a) 1325 °C, (b) 1350 °C, and (c) 1375 °C.

loss and extrinsic loss. The intrinsic losses are mainly caused by lattice vibration modes, while the extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification [10]. The microwave dielectric characteristics and microstructures of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics were determined by sintering conditions and the amount of sintering aid. The dependence of dielectric constant with various amount of Bi_2O_3 addition as function of sintering temperature was illustrated in Fig. 6. As increasing sintering temperature to 1325 °C, the dielectric constant gradually enhanced and then slightly declined thereafter for $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics incorporated with 5 mol% and 10 mol% Bi_2O_3 sintering aids. However, the dielectric constant enhanced linearly for 15 mol% Bi_2O_3 addition. Many factors, such as crystal defects, grain boundary and pores are believed to affect the microwave dielectric loss of ceramics. At sintering temperature of 1375 °C,

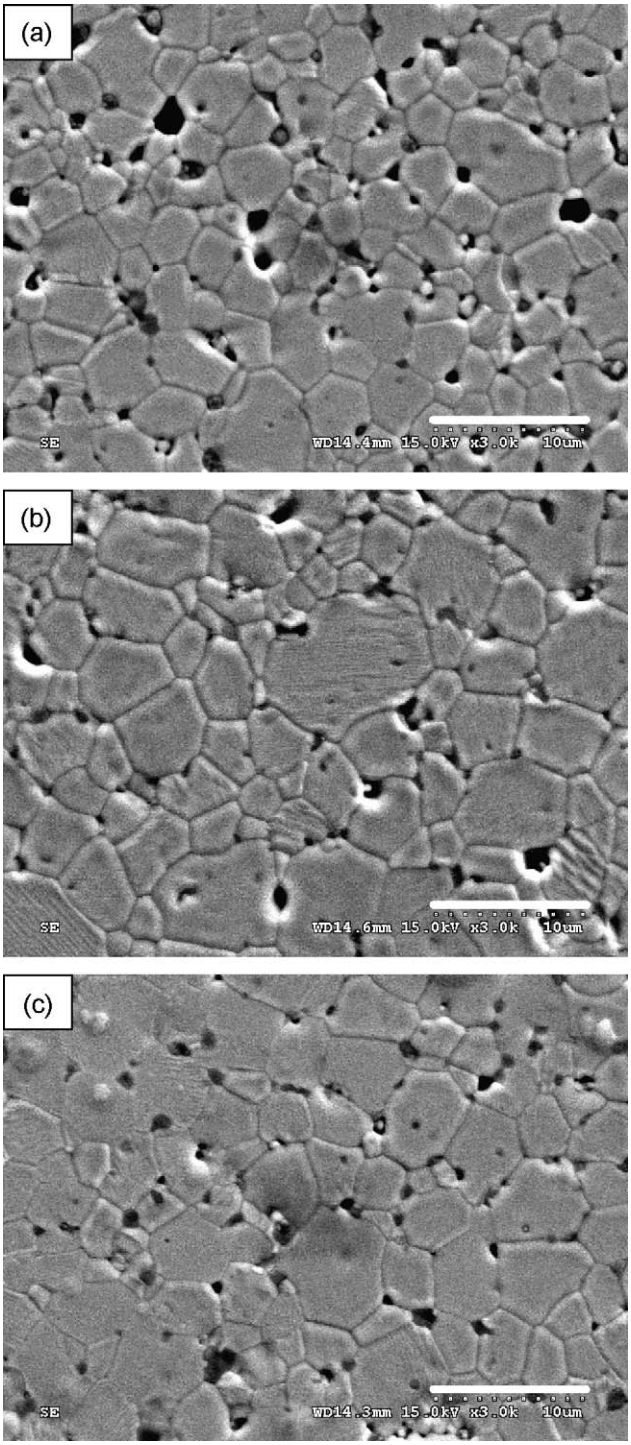

Fig. 4. SEM micrographs of 15 mol% Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at different temperatures: (a) 1325 °C, (b) 1350 °C, and (c) 1375 °C.

the ceramics with 15 mol% Bi_2O_3 additions reached the maximum dielectric constant (ε_r) value of 44. The increase in the dielectric constant was attributed to a higher density as well as a lower porosity. When sintering aid Bi_2O_3 is added in $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics, the dielectric constant as well as apparent density increased gradually with the sintering temperature.

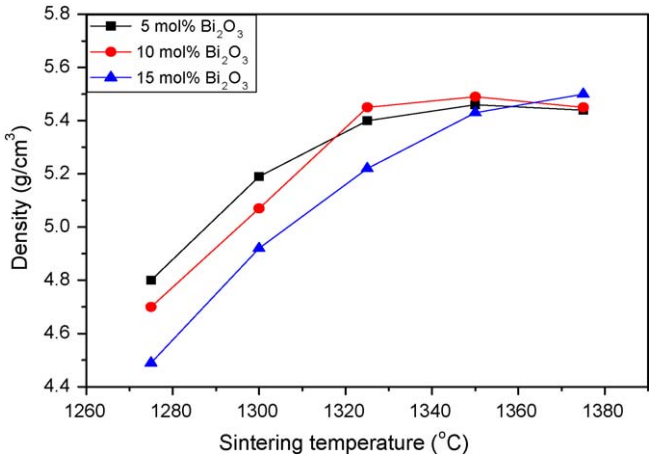

Fig. 5. The dependence of density on sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various amount of Bi_2O_3 additives.

Fig. 7 shows the dependence of quality factor ($Q \times f$) on sintering temperature with doped various amount of Bi_2O_3. For 5 mol% B_2O_3 addition, with increasing sintering temperature, the $Q \times f$ value reached to a maximum of 34,352 GHz at 1325 °C and decreased thereafter. For 10 mol% B_2O_3 addition, the $Q \times f$ value reached a maximum of 23,539 GHz at 1325 °C. Similarly, for 15 mol% B_2O_3 addition, the $Q \times f$ value reached a maximum of 60,231 GHz at 1325 °C and thereafter decreased. Noticeably, the maximum values of $Q \times f$ are found at the sintering temperature of 1325 °C in all specimens. The temperature coefficient of resonant frequency was related to the composition and phase which existed in the ceramic, whereas it was insensitive to the sintering temperature.

Fig. 8 illustrates the temperature coefficient of the resonant frequency (τ_f) of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintering at different sintering temperatures with 5 mol%, 10 mol%, and 15 mol% Bi_2O_3 additions. The literature reported that $La(Mg_{0.5}Ti_{0.5})O_3$ ceramic has a negative τ_f value of −65 ppm/°C [7]. However, the incorporation of Bi_2O_3 would shift τ_f toward positive in this study. As increasing the amount of Bi_2O_3 in the $La(Mg_{0.5}Ti_{0.5})O_3$ ceramic led the value of τ_f

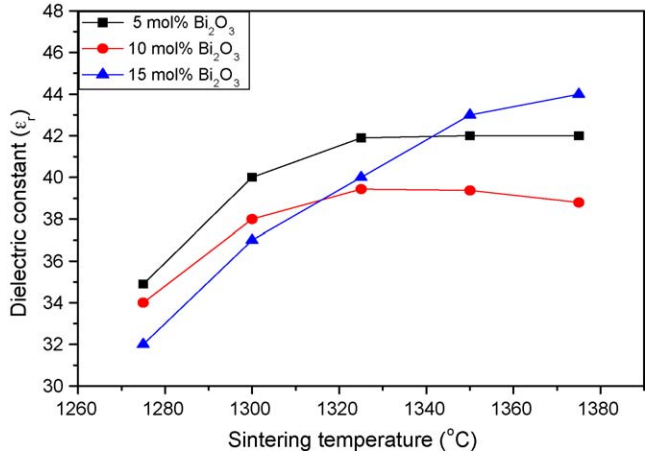

Fig. 6. The dependence of dielectric constant on sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various amount of Bi_2O_3 additives.

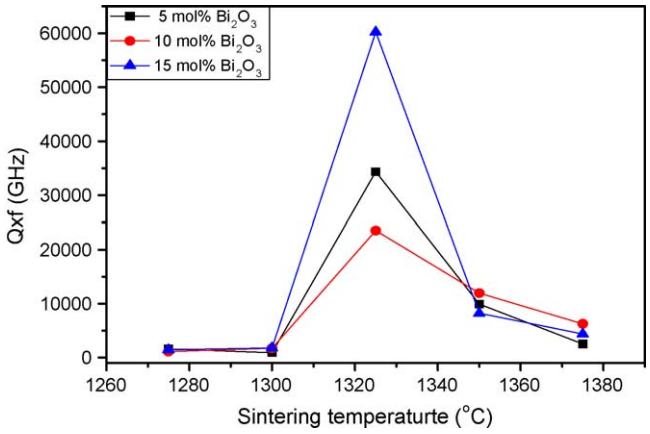

Fig. 7. The dependence of quality factor ($Q \times f$) on sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various amount of Bi_2O_3 additives.

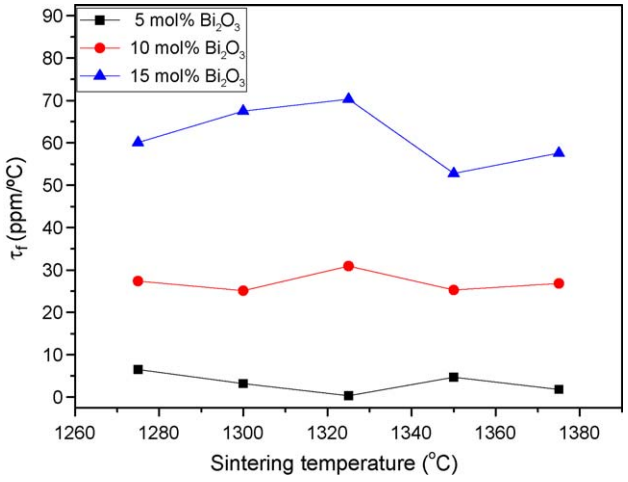

Fig. 8. The dependence of τ_f on sintering temperature of $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various amount of Bi_2O_3 additives.

more positive. For the incorporation of 5 mol% Bi_2O_3 sintering at carious temperatures, the values of τ_f are ranged from 0.3 ppm/°C to 6.5 ppm/°C. A nearly zero τ_f can be obtained for 5 mol% Bi_2O_3 sintering at 1325 °C for 6 h. It implies that nearly zero τ_f can be achieved by appropriately adjusting the amount of Bi_2O_3 additions and sintering temperature.

4. Conclusions

With Bi_2O_3 addition, $La(Mg_{0.5}Ti_{0.5})O_3$ ceramic can be effectively reduced from 1600 °C to 1325 °C. By incorporating in 15 mol% Bi_2O_3, Bi_2O_3-doped $La(Mg_{0.5}Ti_{0.5})O_3$ ceramic revealed the optimum microwave dielectric properties of dielectric constant (ε_r) value of 40.1, a quality factor ($Q \times f$) value of 60,231 GHz, and the temperature coefficient (τ_f) value of 70.1 ppm/°C. During all addition ranges, the relative dielectric constants (ε_r) were different and ranged from 32.0 to 41.9, the quality factors ($Q \times f$) were distributed in the range of 928–60,231 GHz, and the temperature coefficient (τ_f) varies from 0.3 ppm/°C to 70.3 ppm/°C. The quality factor $Q \times f$ was strongly dependent upon the amount of Bi_2O_3 addition and sintering temperature. It is found that incorporating of 15 mol% Bi_2O_3 sintering at 1325 °C can obtain the maximum $Q \times f$ value of 60,231 GHz, and a nearly zero τ_f can be found for doping 5 mol% Bi_2O_3 sintering at 1325 °C.

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