Liquid Phase Effect of Bi_2O_3 and La_2O_3 on Densification, Microstructure and Microwave Dielectric Properties of $MgTiO_3$ Ceramics

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Abstract

$MgTiO_3$ (MTO) ceramics were prepared by means of the solid-state reaction method with the addition of $0.5 - 1.5$ wt% Bi_2O_3 or La_2O_3 as a sintering aid. The effect of Bi_2O_3 or La_2O_3 on the densification, microstructure and microwave dielectric properties of MTO ceramics was investigated. The sintering temperature of MTO ceramics with the addition of Bi_2O_3 or La_2O_3 was lowered to 1200 and 1300 °C, respectively. The lower sintering temperatures were attributed to the liquid phase effect and smaller particle sizes. The microwave dielectric properties showed profound dependence on the sintering temperature as well as the additive concentration. The maximum $Q \times f_0$ values of 71.9 and 136.9 THz were obtained for MTO ceramics with 0.5 wt% Bi_2O_3 and 0.5 wt% La_2O_3, respectively. The microwave dielectric properties of the MTO ceramics showed significant dependence on relative density, average grain size and secondary phases.

Keywords: Microwave ceramics, sintering, dielectric properties, scanning electron microscopy, x-ray diffraction

I. Introduction

Dielectric resonators used at microwave frequencies have been widely investigated owing to the fast growth of microwave telecommunication and satellite broadcasting [1]. Many varieties of dielectric resonator materials have been developed and investigated. Dielectric resonators play a significant role in the miniaturization of microwave components, such as oscillators, amplifiers, tuners and filters [1,2]. The miniaturization of microwave circuits intensely requires a high dielectric constant and low dielectric loss with good temperature stability [2].

$MgTiO_3$ (MTO) is a promising material for dielectric resonator and type I ceramic capacitor applications owing to its excellent microwave dielectric properties and low cost of raw materials [3]. MTO ceramics exhibit an ilmenite structure and belong to the $R\overline{3}$ space group [4]. $MgTiO_3$ ceramics possess a dielectric constant of ε_r ~17, a high $Q \times f_0$ ~ 160 THz at 8 GHz and a negative τ_f value of ~-50 ppm/ °C [5]. In general, the ceramic capacitors are broadly divided into a low permittivity type (type I) with low loss and a high permittivity type (type II). Type I ceramic capacitors exhibit high stability and low losses for resonant circuit application. On the other hand, type II capacitors exhibit a small size with large capacitance and are suitable for filter and decoupling applications. MTO-based ceramics are classically used in the production of type I ceramic multilayer capacitors. As the sintering temperature of MTO is higher than 1450 °C, precious metal/alloy electrodes need to be used. One way to reduce the fabrication cost is to replace the precious metal electrodes with cheaper metal electrodes like Ni and Cu. To use the cheaper metal electrodes, the processing temperature of the MTO has to be reduced [3]. To lower the sintering temperature of the ceramics, three methods are generally adopted: (a) addition of glass phases with a low melting point, (b) chemical processing, and (c) use of smaller initial particle sizes. Further, lowering the sintering temperature with the addition of glass is usually the most effective and least expensive method. Nevertheless, only a few reports are available on the reduction of the sintering temperature of MTO ceramics with different additives. Bernard *et al.* [3] reported the sintering temperature of MTO ceramics as 950 °C with the addition of Li-based salts. Zhang *et al.* [6] reported on MTO ceramics with the addition of 5.0 mol% Bi_2O_3-7.0 mol% V_2O_5 and 6 wt% CuO-Bi_2O_3-V_2O_5, sintered at 875 °C and 900 °C, respectively. Belnou *et al.* studied the addition of bismuth-based additives to lower the sintering temperature of MTO ceramics to below 1000 °C [7]. Nonetheless, the microwave dielectric properties, especially $Q \times f_0$ values, are significantly degraded with these additives. However, no systematic study is available on the addition of smaller initial particle sizes along with La_2O_3 or Bi_2O_3 to MTO ceramics, which motivated the authors to conduct this study. Further, in this study low-melting La_2O_3 and Bi_2O_3 oxides were chosen to reduce the sintering temper-

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ature of MTO ceramics because La_2O_3 and Bi_2O_3 form liquid phases at 1300 °C and 740 °C, respectively. Hence, in the present study we have investigated (i) the effect of La_2O_3 and Bi_2O_3 and (ii) influence of smaller initial particle sizes on crystal structure, densification, microstructure and microwave dielectric properties of pure and La_2O_3- and Bi_2O_3-added MTO ceramics.

II. Experimental Procedure

The $MgTiO_3$ samples were prepared by means of the conventional solid-state route from high-purity oxide powders (> 99.99 %): MgO and TiO_2. The starting materials were mixed according to the stoichiometry of $MgTiO_3$ and milled in distilled water for five hours in a planetary ball mill (Fritsch GmbH, Germany). The prepared mixtures were dried and calcined at 1100 °C for two hours in air. The calcined powders were re-milled for 10 hours. Subsequently, different wt% of La_2O_3 or Bi_2O_3 were added to MTO ceramics and these were then further milled for two hours. The as-milled powders were uniaxially pressed under 2000 kg/cm^2 into pellets with dimensions of 10 mm in diameter and 4 – 5 mm in thickness. The MTO ceramics with added La_2O_3 or Bi_2O_3 were sintered in the range of 1100 – 1400 °C for three hours.
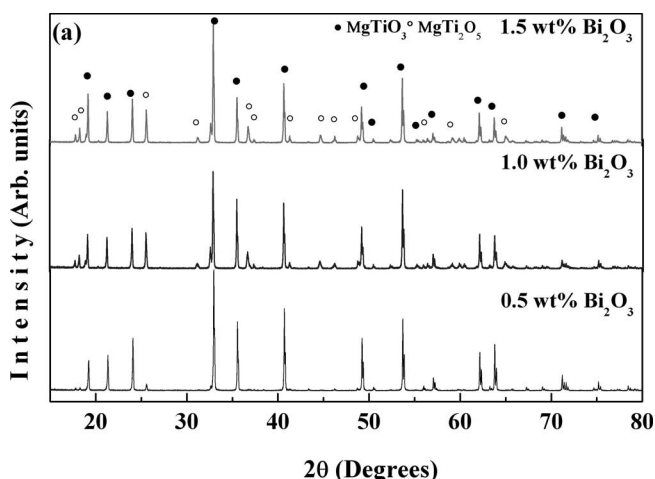

Fig. 1 a: XRD patterns of the MTO ceramics with different added wt% Bi_2O_3 and sintered at 1200 °C.
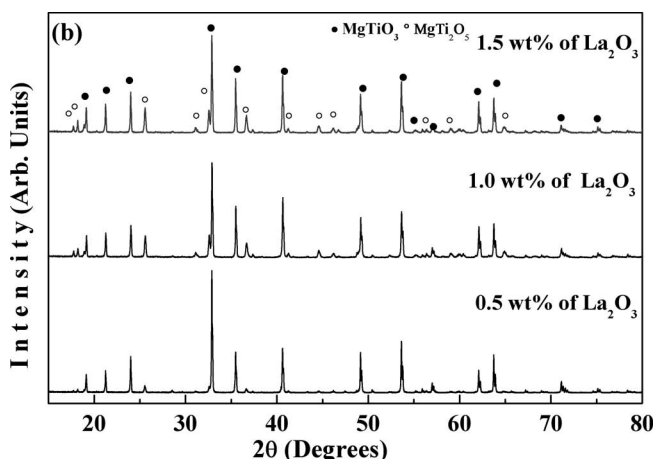

Fig. 1 b: XRD patterns of the MTO ceramics with different added wt% La_2O_3 and sintered at 1300 °C.

The phase purities of the sintered MTO ceramics were examined based on XRD patterns recorded with a Rigaku high-power x-ray diffractometer (RINT 2500 system TTRAX) with CuKα radiation (λ = 1.5406 Å). The surface morphology and chemical composition of the sintered MTO ceramics were obtained with a scanning electron microscope (Leo 1430vp) and energy dispersive spectroscopy (EDS). The relative densities of the sintered MTO ceramics were measured with the Archimedes method. The dielectric constant ε_r and quality factors $Q \times f_0$ of the samples at microwave frequencies were measured using the Hakki and Coleman dielectric resonator method, as modified and improved by Courtney [8, 9].

III. Results and Discussions

(1) Structural analysis

To examine the effect of these additives on the crystal structure of the MTO ceramics, XRD patterns of the samples were obtained. Figs. 1a and 1b show the XRD patterns of MTO ceramics with the addition of Bi_2O_3 ($x = 0.5$, 1.0 and 1.5 wt% Bi_2O_3), sintered at 1200 °C, and La_2O_3 ($y = 0.5$, 1.0 and 1.5 wt% La_2O_3), sintered at 1300 °C, respectively. It was observed that all the samples exhibited trigonal $MgTiO_3$ as the main crystalline phase (ICDD 06 – 0464) and $MgTi_2O_5$ as the minor secondary phase. Moreover, with an increase in wt% of the additives, the percentage of secondary phases also increased. However, the MTO ceramics with the addition of $x = y = 0.5$ wt% of Bi_2O_3 or La_2O_3 exhibited only two negligible peaks of $MgTi_2O_5$. With the further increase in the wt% of the additive, the number of secondary phases increased in addition to their peak intensities. $MgTi_2O_5$ is usually formed as a minor phase and is difficult to eliminate completely from the samples prepared according to the mixed oxide route. Furthermore, the determined lattice constants of the MTO ceramics with these additives revealed that there is no deviation of the values compared to those of pure MTO ceramics, because the ionic radii of the La^{3+} and Bi^{3+} are larger than those of Mg^{2+} and Ti^{4+}. This implies that these additives do not enter the crystal lattice of the MTO matrix, but remain at the grain boundary.

(2) Microstructure and relative density

To determine the effect of these additives on the microstructure of the MTO ceramics, micrographs of the samples were obtained with SEM. Fig. 2 (a - c) and Fig. 3 (a - c) show the SEM images of the MTO ceramics with the addition of $x = 0.5 – 1.5$ wt% Bi_2O_3 and $y = 0.5 – 1.5$ wt% La_2O_3, respectively. In both the cases, it was observed that all the samples were crack-free and exhibited uniform dense microstructures. The mean grain sizes of the samples with added Bi_2O_3 were found to decrease with an increase in Bi_2O_3 wt% whereas the MTO ceramics with La_2O_3 exhibited larger average grain sizes with an increase in the additive concentration. In addition, the samples with the addition of $x = 0.5$ wt% exhibited larger average grain sizes with identical microstructures while the samples with $y = 1.5$ wt% exhibited uniform microstructures with larger average grain sizes. Moreover, in the case of MTO ceramics with the addition of
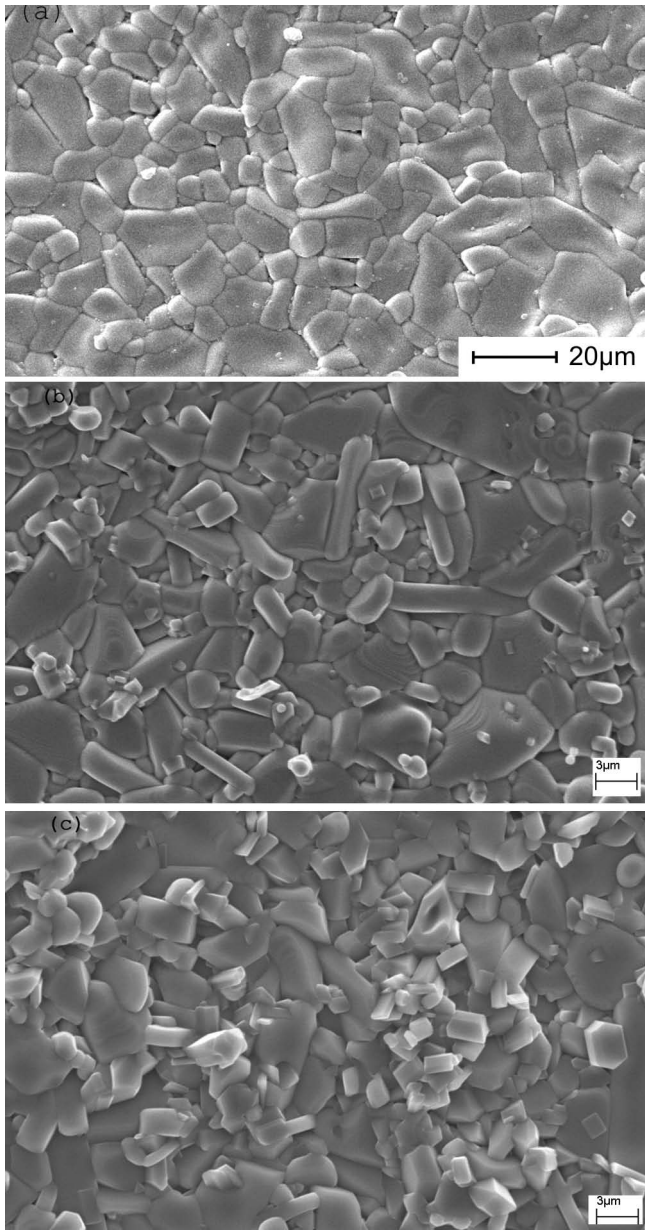
growth and increase the average grain size whereas the La$_2$O$_3$ addition enhanced both grain growth and the average grain size of the MTO ceramics.
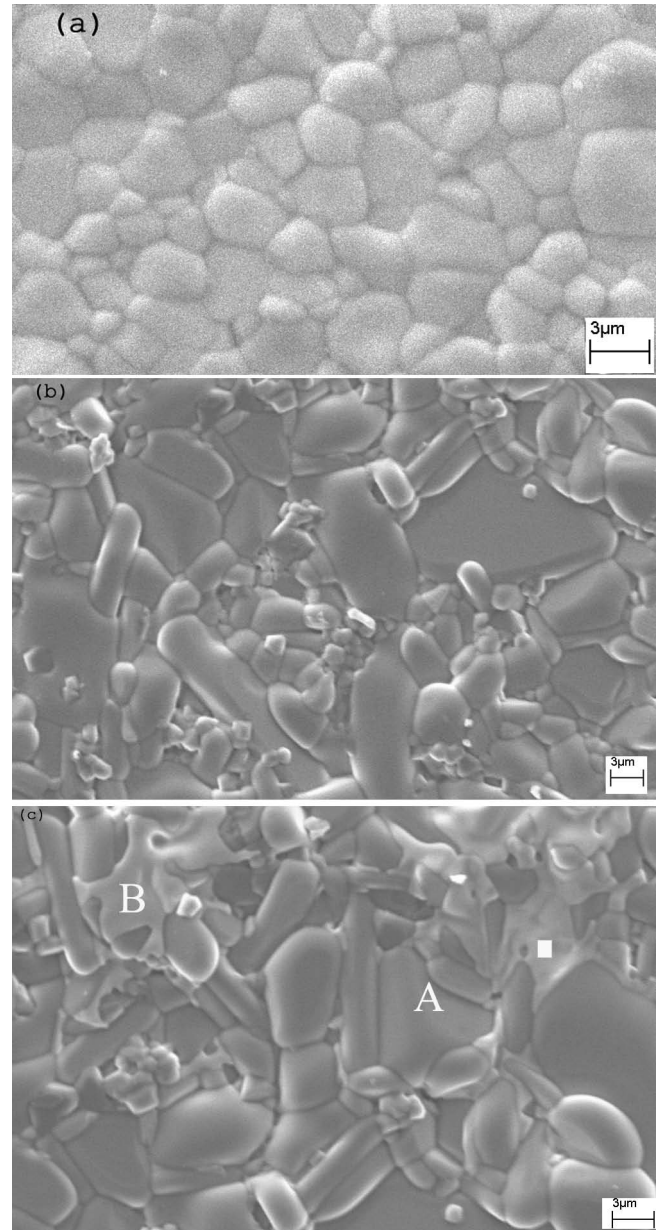

Fig. 2 : SEM images of the MTO-Bi$_2$O$_3$ (x wt%) ceramics with (a) $x = 0.5$, (b) $x = 1$ and (c) $x = 1.5$.

Fig. 3 : SEM microstructures of the MTO- La$_2$O$_3$ (y wt.%) ceramics with (a) $y = 0.5$, (b) y = 1 and (c) $y = 1.5$.

$y =1.5$ wt%, smaller grains were observed within the grain boundaries of the large grains. Further, as the y wt% increases, the grain morphology of the dense MTO ceramics exhibited two different types of grains: at the grain boundary of the large grains, a segregation of white-coloured phase was observed. In order to understand the chemical composition of this contrast phase, EDS analysis was performed. The chemical composition for MTO + y = 1.5 wt% (Fig. 3c) contrast phase based on the EDS spectra is shown in Fig. 3d. The larger grains (spot A) exhibited the chemical composition of MgTiO$_3$, whereas the white layer (spot B) showed the chemical composition of La$_2$Ti$_2$O$_7$; a similar effect was observed by Ferreira *et al.* [10]. However, this phase could not be identified from the XRD patterns because the detection of minor phases by means of XRD is extremely difficult. The average grain sizes of the samples were in the range of $8.1-2.5$ μm and $10.2-3.2$ μm with the addition of Bi$_2$O$_3$ and La$_2$O$_3$, respectively, which indicates that the addition of Bi$_2$O$_3$ did not promote grain
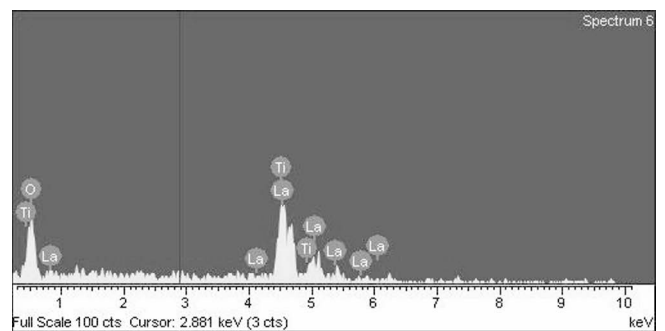

Fig. 3 d: EDS spectra of MTO ceramics with $y = 1.5$ added.

In addition, the uniform large average grain size of the MTO ceramics obtained with added $x = 0.5$ wt% is due to

the identical grain growth, microstructure and the presence of a small amount of $MgTi_2O_5$ phase. The reduction in the average grain size and non-uniform microstructures can be attributed to the presence of secondary phases, and the segregation of liquid phase observed within the grain boundaries. Further, an increase in x wt% enhanced the growth of $MgTi_2O_5$, which resulted in smaller grain sizes and non-uniform grain growth. In the case of the MTO ceramics with added La_2O_3, in addition to $MgTi_2O_5$ phase, $La_2Ti_2O_7$ was also observed, which enhanced the grain size and grain growth (see Fig. 3c). Microstructure analysis reveals that the nature of the additive and its concentration plays an important role during the development of a uniform microstructure and the average grain sizes of the MTO ceramics.
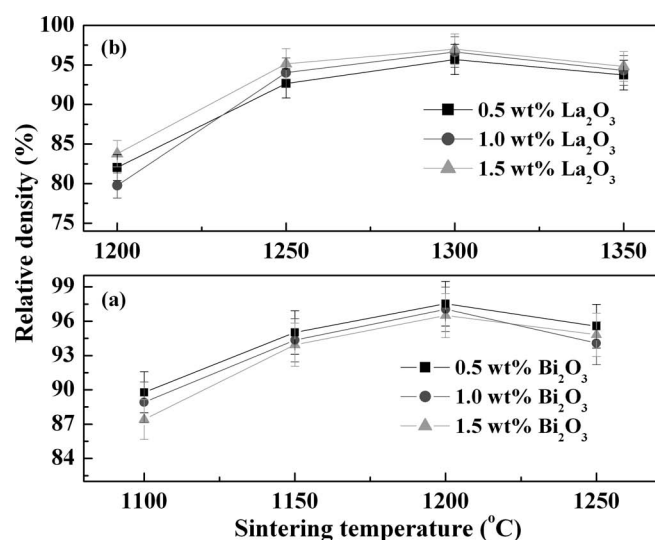

Fig. 4: Variation in relative densities of the MTO ceramics as a function of sintering temperatures with the addition of different wt% (a) Bi_2O_3, (b) La_2O_3.

To understand the effect of these additives on the densification of MTO ceramics, the relative densities of MTO ceramics mixed with different weight percentages of Bi_2O_3 and La_2O_3 were measured. Thevariation in relative densities of MTO ceramics with added Bi_2O_3 and La_2O_3 as a function of sintering temperatures are shown in Figs. 4a and 4b, respectively. While the MTO ceramics with added Bi_2O_3 shows a continuous increase in relative density from 86.5 to 97.5 % with an increase in sintering temperature from 1100 °C to 1200 °C.The maximum of 97.5 % of the theoretical density was obtained for the sample with the addition of x = 0.5 wt%. Further, the relative density was found to decrease with an increase in x wt%. The decrease in the relative densities with higher x wt% can be attributed to the non-uniform grain growth and the presence of secondary and liquid phases (Figs. 2b and 2c). Nevertheless, the decrease in density above 1200 °C may be due to the evaporation of Bi_2O_3, which causes the non-uniform growth (Fig. 2c). The addition of Bi_2O_3 reduced the sintering temperature from 1350 °C to 1200 °C. However, the MTO ceramics with La_2O_3 revealed the maximum density of 96.9 % at 1300 °C. In addition at a given temperature, the relative densities of the samples increased with an increase in y wt%. The increase in relative densities with the increase in y wt% can be correlated to the enhancement of uniform grain growth and average grain size. Ferreira *et al.* [10] reported the sintering temperature of the MTO ceramics with added La_2O_3 as 1350 °C. Nevertheless, in the present study, the MTO ceramics with added La_2O_3 achieved higher densities at 1300 °C, whereas the pure MTO ceramics exhibited a maximum density of 96.4 % at 1350 °C. These results confirm that the densification of MTO ceramics without the sintering aid is considerably more difficult.
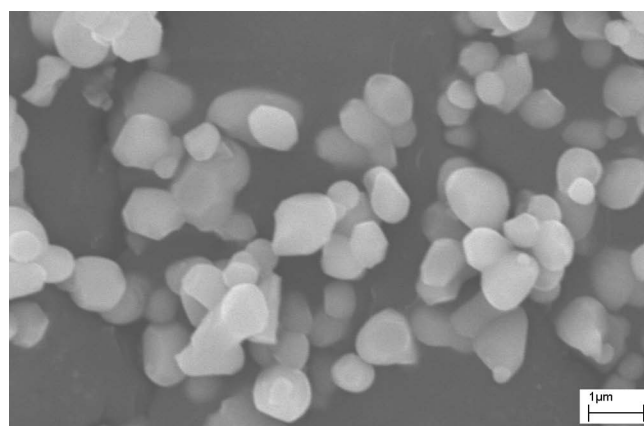

Fig. 5: SEM microstructure of the pure MTO ceramics milled for 10 hours.

The addition of La_2O_3 could not reduce the sintering temperature much because La^{3+} controls the grain growth and the solubility limit for La in MTO ceramics could be very low because of the $La_2Ti_2O_7$ secondary phase. In the present study, the obtained lower sintering temperatures are a collective effect of liquid phase and smaller initial particle sizes. The effects of these additives and sintering temperature on the improvement of the relative density and microstructure can be described by the following mechanism: In liquid phase sintering, the liquid spreads to cover the solid surfaces, which will be separated by the liquid bridge. This decreases the friction between the MTO particles and exerts a capillary force, which can be used to rearrange the particles more easily and enhance the densification process to get maximum packing [11]. Furthermore, sintering becomes faster as the particle size decreases, since the diffusion distances are shorter and curvature stresses longer. In the arrangement stage, a small particle size improves the role of rearrangement because of a large capillary force even though the amount of friction is increased. Similarly, in the solution re-precipitation stage, a small particle size improves the densification rate [12]. Fig. 5 shows the initial particle sizes of the MTO ceramics milled for 10 hours. It shows that the average initial particle size is around 700 nm. However, the pure MTO ceramics exhibited maximum densities of 82 % and 92 % of theoretical densities sintered at 1200 °C and 1300 °C respectively, and the pure MTO ceramics exhibited maximum density of 96.4 % at 1350 °C for three hours. This comparison shows that the obtained maximum densities are the combined effect of the liquid phase and initial particle size because the initial particle size alone did not increase the densities of the MTO ceramics.

(3) Microwave dielectric properties

To observe the influence of these additives on the microwave dielectric properties of MTO ceramics, we measured the dielectric constant and quality factor at microwave frequencies for all the samples as shown in Fig. 6. In both cases, it is clear to see that the dielectric constant ε_r as a function of sintering temperature followed a similar trend as that of the relative density as a function of sintering temperature, suggesting that the dielectric constants of the investigated MTO ceramics can be enhanced by increasing densification, which results in a reduction in porosity. The dielectric constants of the MTO ceramics with added Bi$_2$O$_3$ ranged from 14.7 to 16.6 whereas the samples with added La$_2$O$_3$, exhibited a range of 12.8 to 16.9. The lower values obtained for the dielectric constants can be attributed to the lower relative densities and fewer secondary phases. The resonant frequency of the measured samples is around 10.5 GHz.
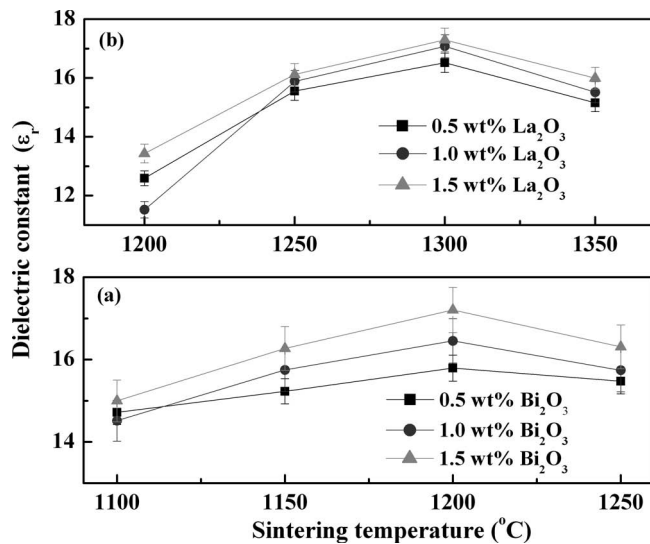

Fig. 6: Variation in dielectric constants of the MTO ceramics as a function of sintering temperatures with the addition of different wt% (a) Bi$_2$O$_3$, (b) La$_2$O$_3$.

The product of the quality factor Q and the resonance frequency f_o is the tool for evaluating the performance of a dielectric resonator material. The variation in $Q \times f_0$ of the MTO mixed with Bi$_2$O$_3$ and La$_2$O$_3$ as a function of sintering temperature is shown in Fig. 7. In the case of the MTO ceramics with Bi$_2$O$_3$, the $Q \times f_0$ values increased up to 1200 °C, then decreased thereafter, following the same trend as that of the relative density and ε_r as a function of the sintering temperature. A maximum $Q \times f_0$ value of 71.9 *THz* (at 10.5 *GHz*) is obtained for the sample with $x = 0.5$ wt%, sintered at 1200 °C. In addition, $Q \times f_0$ values were found to decrease with an increase in x wt%. Kim *et al.* [13] proposed that the increase in the dielectric loss in the (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ ceramics with the addition of Bi$_2$O$_3$ is due to the substitution of Bi^{3+} ions in Ti site, which creates oxygen vacancies. However, this loss mechanism is not applicable to the present situation since the ionic radii of Bi^{3+} ion in the ilmenite structure are 1.03 Å, because both A and B sites belong to the co-ordinance 6. Hence the Bi^{3+} ion cannot be substituted in the Mg^{2+} (0.72 Å) and Ti^{4+} (0.605 Å) sites. This would complement the ob-

tained lattice constants calculations that these additives did not enter into the MTO matrix but remained at the grain boundary. The decrease in the Qxf$_0$ values of the MTO ceramics with the higher concentration of Bi$_2$O$_3$ may be due to an increase in the oxygen vacancies, which increase the anharmonic interactions, lower densities and a decrease in the average grain size.
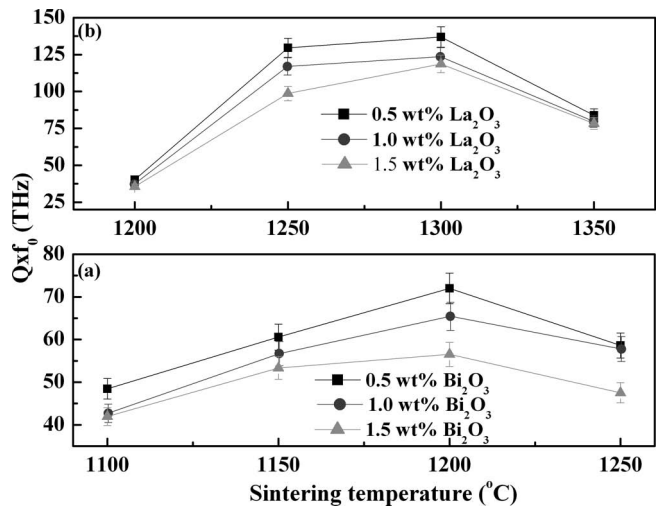

Fig. 7: Variation in $Q \times f_0$ of MTO ceramics as a function of sintering temperatures with the addition of different wt% (a) Bi$_2$O$_3$, (b) La$_2$O$_3$.

In the case of the MTO ceramics with La$_2$O$_3$, the $Q \times f_0$ values were found to increase with an increase in sintering temperature up to 1300 °C and decrease thereafter. The maximum values of $Q \times f_0$ (136.9 *THz*) were obtained for the MTO ceramics with $y = 0.5$ wt%, sintered at 1300 °C. In addition, it was also observed that with an increase in the y wt% the $Q \times f_0$ values decreased drastically although there is an improvement in the density and an increase in the average grain size. The lower $Q \times f_0$ values were due to the presence of La$_2$Ti$_2$O$_7$ and MgTi$_2$O$_5$, which result in the absorption of electromagnetic radiation. The MgTi$_2$O$_5$ exhibits inferior microwave dielectric properties, which deteriorate in the microwave dielectric loss of the MTO ceramics [14]. The best $Q x f_0$ values obtained from the samples added with $y = 0.5$ wt% may be due to the absence of La$_2$Ti$_2$O$_7$ in these samples, which is confirmed in the EDS spectra. Although the La$_2$O$_3$-TiO$_2$ system has the ability to form eutectic liquids around 1300 °C, this was not observed in the present study. Further, it can be concluded that the La^{+3} also cannot be substituted for Mg^{2+} and Ti^{4+} ion sites because the ionic radii of La^{+3} (1.061 Å) are larger that those of Mg^{2+} and Ti^{4+} ion sites. In the case of the MTO ceramics with La$_2$O$_3$, the microwave dielectric loss was heavily influenced by the secondary phases and is independent of grain size and relative densities. However, the observed $Q \times f_0$ values obtained with this additive were found to be lower compared to those of pure MTO ceramics sintered at 1350 °C for three hours. The pure MTO ceramics exhibited ε_r of 18.52 and $Q \times f_0$ 162.3 *THz*. In both the cases, it is clearly observed that there is not much variation in the ε_r values whereas the $Q \times f_0$ values are heavily influenced because the higher concentrations of these additives create local impurities, defects and secondary phases, which result in

absorption of electromagnetic radiation, leading to the increase in microwave dielectric loss. The addition of Bi_2O_3 and La_2O_3 reduced the sintering temperature and exhibited maximum relative densities, but could not improve the microwave dielectric loss as compared with that of pure MTO ceramics.

The microwave dielectric losses arise from the two mechanisms (i) intrinsic and (ii) extrinsic losses [15, 16]. Intrinsic losses arise owing to the enharmonic forces that mediate the interaction between crystal lattice modes and electromagnetic radiation, leading to damping of the optical phonons. On the other hand, the extrinsic losses are caused by the extended dislocations, grain boundaries, porosity, oxygen vacancies and secondary phases, which are heavily dependent on the processing conditions. These losses are caused mainly by the dipolar relaxation of the defect-oriented polarizations concentrated at the interfaces. Generally, the specimen with larger grain size was expected to have a high $Q \times f_0$ because the grain growth reduces the grain boundary area [17]. From the present study, it is clearly evident that the microwave dielectric properties of MTO ceramics are strongly influenced by the additives and their concentrations. Further, it is significant to note that the MTO ceramics with these additives exhibited the best microwave dielectric properties at lower sintering temperatures, which qualify these materials for resonator and type I capacitor applications.

IV. Conclusions

The effects of Bi_2O_3 or La_2O_3 on the densification, microstructure and microwave dielectric properties of MTO ceramics were investigated. The observed results suggested that the inclusion of these additives effectively reduces the sintering temperature of MTO ceramics while significantly improving their density and microstructure. The reduction in the sintering temperature is a combined effect of both smaller initial particle sizes and the liquid phase effects. In both cases, relative density and dielectric constant follow the same trend as a function of temperature as well as the wt% of the additive concentration whereas the $Q \times f_0$ values are affected profoundly. The obtained properties of the MTO ceramics sintered at the lower temperatures are promising for DR and type I ceramic capacitor applications.

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