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The influence of sintering aids for $Nd(Mg_{0.5}Ti_{0.5})O_3$ microwave dielectric ceramics properties

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Abstract

The influence of various sintering aids on the microwave dielectric properties and the structure of $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics were investigated systematically. B_2O_3, Bi_2O_3, and V_2O_5 were selected as liquid-phase sintering aids to lower the sintering temperature. The sintered $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and microwave dielectric properties. The sintering temperature of $Nd(Mg_{0.5}Ti_{0.5})O_3$ microwave dielectric ceramics is generally high, about 1500 °C. However, the sintering temperature was significantly lowered about 175 °C from 1500 °C to 1325 °C by incorporating in 10 mol% B_2O_3 and revealed the optimum microwave dielectric properties of dielectric constant (ε_r) value of 26.2, a quality factor ($Q \times f$) value of 61,307 (at 9.63 GHz), and τ_f value of −45.5 ppm/°C. $NdVO_4$ secondary phase was observed at 10 mol% V_2O_5 addition in the sintering temperature range of 1300–1325 °C, which led the degradation in microwave dielectric properties. The microwave dielectric properties as well as grain sizes, grain morphology, and bulk density were greatly dependent on sintering temperature and various sintering aids. In this study, it is found that $Nd(Mg_{0.5}Ti_{0.5})O_3$ incorporated with 10 mol% B_2O_3 with lower sintering temperature and excellent dielectric microwave properties may be suggested for application in microwave communication devices. The use of liquid-phase sintering, the liquid formed during firing normally remains as a grain boundary phase on cooling. This grain boundary phase can cause a deterioration of the microwave properties. Therefore, the selection of a suitable sintering aid is extremely important.

Keywords: A. Powder: solid-state reaction; A. Sintering; C. Dielectric properties

1. Introduction

Due to rapid development in the microwave communication system, satellite broadcasting system, as well as wireless mobile systems, has become more important for the miniaturization of microwave device, such as oscillators, band pass filters, duplexers and global positioning systems (GPS) patch antennas [1,2]. To miniaturize the devices and for the systems to work with high efficiency and stability, the materials for microwave resonators must be excellent in the following three dielectric characteristics. The first characteristic is a high dielectric constant ($\varepsilon_r > 20$). The use of high dielectric constant materials can effectively reduce the size of resonators since the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_0) in vacuum ($\lambda = \lambda_0/\sqrt{\varepsilon_r}$). The second is a high quality factor ($Q \times f$) value ($Q > 5000$). This is required to achieve high frequency selectivity and stability in microwave transmitters and receiver components. The third is a near zero temperature coefficient of resonant frequency (τ_f) for dielectric resonators and microwave device substrates [3,4]. Small temperature coefficients of the resonant frequency ensure the stability of the microwave components at different working temperatures. Using two or more compounds with negative and positive temperature coefficients to form a solid solution mixed phases is the most promising method of obtaining a zero temperature coefficient of the resonant frequency. Because most dielectric ceramics with high dielectric constant have positive τ_f value [5], searching for materials with a high dielectric constant, a high Q and a negative τ_f is necessary to achieve this goal. Low temperature solid-state synthesis is an

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approach that shows great promise for the synthesis of materials with unusual interesting properties. 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 [6–9]. 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 procedure, which was expensive and time consuming. Therefore, the selection of non-glass addition with low melting point is extremely important.

Since B_2O_3, Bi_2O_3, and V_2O_5 are commonly used as a liquid-phase flux and have been shown to accomplish a substantial sintering temperature reduction [10,11], it was selected as a sintering aid in present study. The objective of this study is to develop a new dielectric material which has high dielectric constant, high quality factor and near to zero τ_f by incorporating 10 mol% of B_2O_3, Bi_2O_3, and V_2O_5 into $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics. The resultant microwave dielectric properties were measured based upon the densification, the X-ray diffraction patterns and the microstructures of the ceramics.

2. Experimental procedure

Specimen powders were prepared by a conventional solid-state method. High-purity oxide powders (>99.9%): Nd_2O_3, MgO and TiO_2 were used as raw materials. The powders were weighed according to the composition $Nd(Mg_{0.5}Ti_{0.5})O_3$, and were ground in distilled water for 12 h in a balling mill with agate balls. Prepared powders were dried and calcined at 1100 °C for 2 h in air. The calcined powers were mixed as desired composition $Nd(Mg_{0.5}Ti_{0.5})O_3$ with 10 mol% of different sintering aids (B_2O_3, Bi_2O_3, and V_2O_5) and re-milled for 12 h. These fine powders were mixed with the organic binder (PVA) and pressed at 25 kg/cm^3 into pellets with dimensions of 11 mm diameter and 5 mm thickness. These pellets were sintered at temperatures of 1300–1375 °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). The crystalline phase of sintered ceramics was identified by X-ray diffraction (XRD, RIGAKU D/max 2.B) with CuKα radiation (λ = 1.5418 Å at 40 kV and 30 mA) and scanned from 20° to 70° 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 [12,13]. 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 from 30 °C to 80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (f), and is defined by $\tau_f = f_2 - f_1 / f_1(T_2 - T_1)$ where, f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 presents the XRD patterns of $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with (a) 10 mol% B_2O_3, (b) 10 mol% Bi_2O_3, and (c) 10 mol% V_2O_5 additive sintered at different temperatures 1300 °C, 1325 °C, 1350 °C and 1375 °C, respectively, for 6 h. Identical XRD patterns of Fig. 1(a) and (b) were observed have not change significantly with sintering temperatures in the range of 1300–1375 °C. No secondary phases for incorporating with B_2O_3 or Bi_2O_3 are observed since detection of a minor phase by X-ray is extremely difficult. Whereas second phase is detected for $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics incorporated with V_2O_5, which is shown in Fig. 1(c). The intensity of the second phase peak decreases with increasing sintering temperature.

The SEM images of as-fired surface from the specimens of $Nd(Mg_{0.5}Ti_{0.5})O_3$ incorporated with various sintering aids are illustrate in Figs. 2–4. As shown in Fig. 2, the B_2O_3-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with sintering temperatures of 1300–1375 °C for 6 h, the porosity decreased with increasing sintering temperature. Degradation in grain uniformity and abnormal grain growth started to appear for ceramics specimens at sintering temperatures of 1350 °C, Moreover, at the

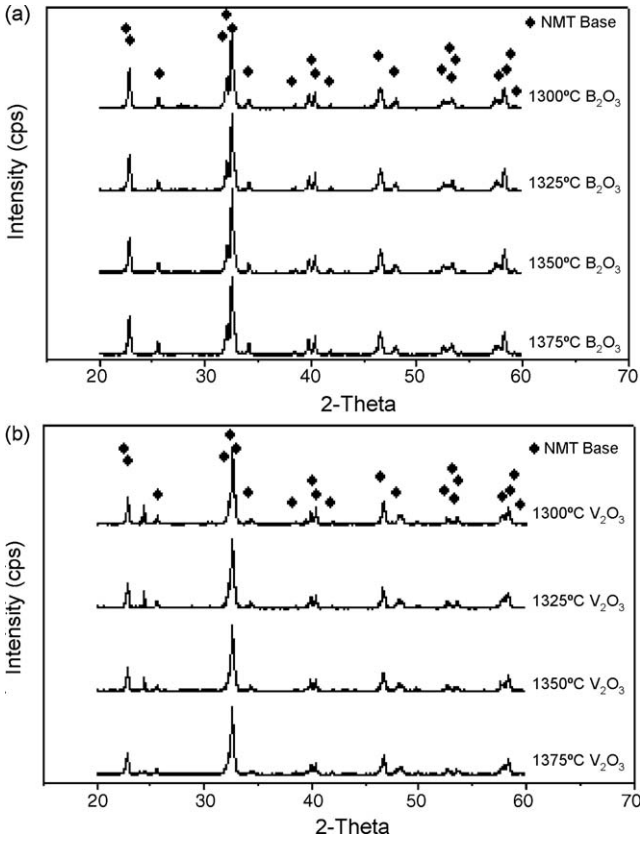

Fig. 1. XRD patterns of $Nd(Mg_{0.5}Ti_{0.5})O_3$ sintered at various temperatures for 6 h with (a) 10 mol% B_2O_3 and (b) 10 mol% V_2O_5 additives.

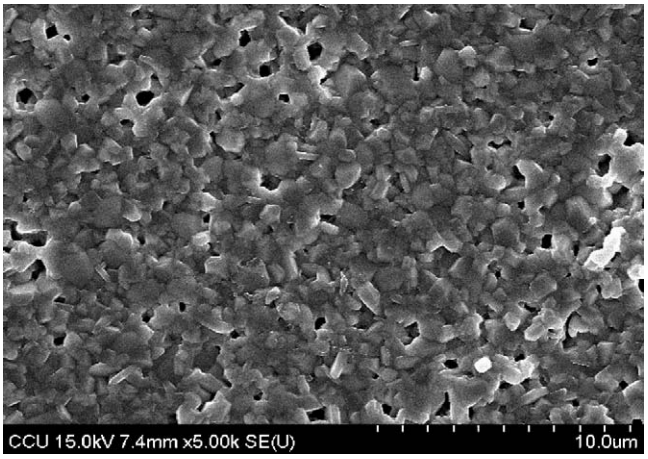

Fig. 2. SEM micrographs of 10 mol% B_2O_3-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at 1350 °C for 6 h.

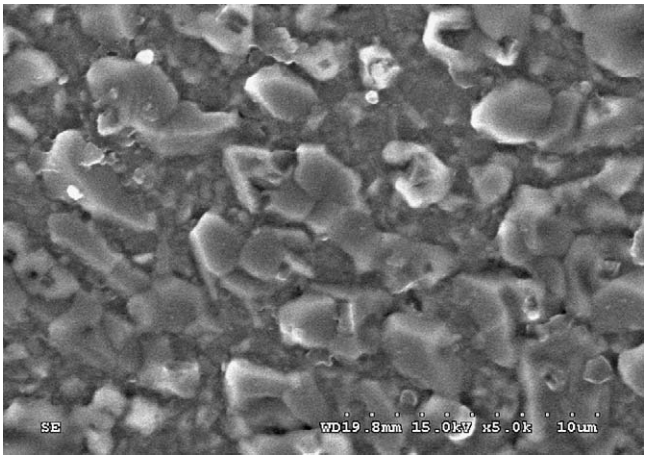

Fig. 3. SEM micrographs of 10 mol% Bi_2O_3-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at 1350 °C for 6 h.

sintering temperature of 1375 °C, the grain is growth. The grain size increased with increasing sintering temperature is due to the liquid-phase effect, which may damage microwave dielectric properties. Fig. 3 shows the SEM micrographs of 10 mol% Bi_2O_3-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics sintered at 1350 °C for 6 h. With increasing sintering temperature, the porosity decreased. However, non-uniformity grains and abnormal grain growth appeared in the sintering temperatures range of 1350–1375 °C. These behaviors may directly affect the microwave dielectric properties, which might lead to degradation in the microwave dielectric properties. Generally, abnormal grain growth is due to two factors: (1) the effects of impurities in the grain boundaries and (2) an anisotropic grain boundary energy. In this study, we speculated that abnormal grain growth derives mainly from impurities in the grain boundaries. These impurities are sintering aids, *i.e.* Bi_2O_3. The SEM micrographs of 10 mol% V_2O_5-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with sintering temperatures of 1300 °C and 1350 °C are shown in Fig. 4. When sintering aid of V_2O_5 was added, the $NdVO_4$ second phase appeared at sintering temperatures of 1300 °C. Obviously, there are a number of needle-like $NdVO_4$

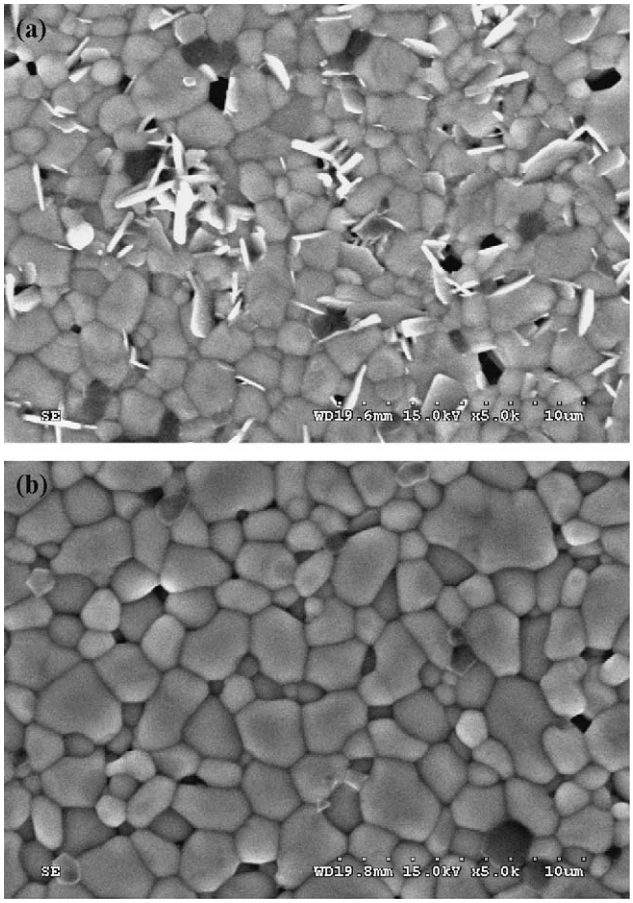

Fig. 4. SEM micrographs of 10 mol% V_2O_5-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics at sintering temperatures of (a) 1300 °C and (b) 1350 °C for 6 h.

secondary phase precipitated on grain boundaries. However, as sintering temperature at 1350 °C, the second phases were vanished and the uniformly grown grains were observed. High sintering temperature may lead the secondary phase to incorporate with matrix material ($Nd(Mg_{0.5}Ti_{0.5})O_3$). The V_2O_5-doped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics were already dense at 1350 °C while the undoped $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with high relative density required high sintering temperature to over 1500 °C.

Fig. 5 shows the bulk density of $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with various sintering aids at different temperatures. In all specimens, the densities increased with increasing sintering temperature due to the decrease in the number of pores as observed in SEM. However, too high sintering temperature would cause abnormal grain growth resulted in a decrease in density. Moreover, increase the sintering temperature would enhance the grain growth resulting in an increase of the density. At 1375 °C, the ceramics with 10 mol% B_2O_3 addition reached the optimal bulk density. But the bulk density increased till to 1375 °C at higher temperature due to abnormal grain growth which may affect the dielectric loss of the ceramics. A maximum density of 6.4 g/cm^3 was obtained for $Nd(Mg_{0.5}Ti_{0.5})O_3$ with 10 mol% B_2O_3 sintered at 1375 °C for 6 h. It implied that B_2O_3 can effectively enhance bulk density than the other sintering aids (Bi_2O_3 and V_2O_5).

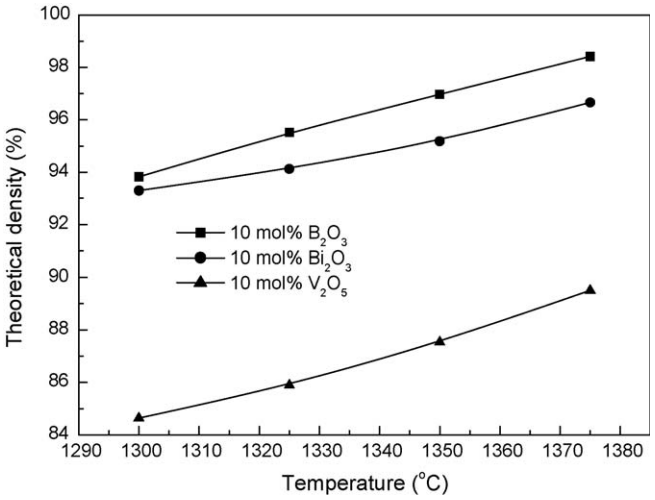

Fig. 5. The dependence of density on sintering temperature for $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with 10 mol% B_2O_3, Bi_2O_3, and V_2O_5 additives.

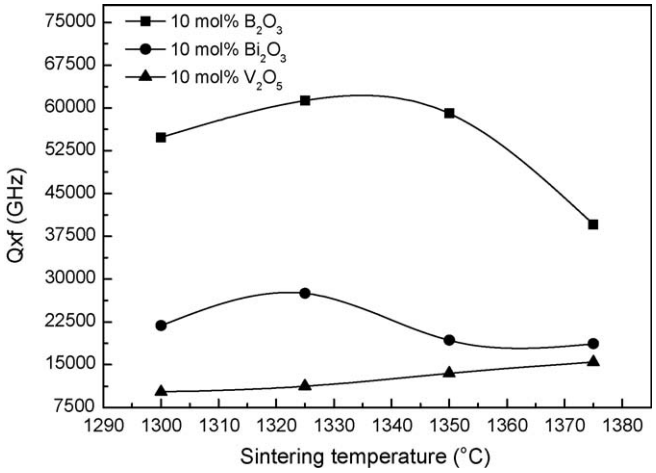

Fig. 7. The dependence of quality factor ($Q \times f$) on sintering temperature for $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with 10 mol% B_2O_3, Bi_2O_3, and V_2O_5 additives.

The microwave dielectric characteristics and microstructures of $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics were determined by the sintering conditions and the sintering aid. The dependence of dielectric constant on sintering temperature with doped different sintering aids is illustrated in Fig. 6. As increasing sintering temperature to 1325 °C, the dielectric constant of B_2O_3-doped sample increase slightly than Bi_2O_3-doped sample, however the increase in sintering temperature to 1350 °C caused the abnormal grain growth and degraded its dielectric constant. The increase in the dielectric constant was attributed to a higher density as well as a lower porosity. When V_2O_5 is added, the dielectric constant increased linear as the sintering temperature increased, as the crystalline grain is relatively dense. With decreasing the sintering temperature, the decrease in dielectric constant is due to $NdVO_4$ second phase appeared.

There are a number of factors that affect the microwave dielectric loss which can be divided into two kinds, the intrinsic 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 or porosity [14]. Fig. 7 shows the dependence of quality factor ($Q \times f$) on sintering temperature with doped different sintering aids. For B_2O_3 addition, with increasing sintering temperature, the $Q \times f$ value was found to increase a maximum and thereafter decreased its value. As increasing sintering temperature to 1325 °C, the $Q \times f$ reached a maximum value of 61,307 (at 9.63 GHz) and thereafter decreased. The similar behavior was also found in Bi_2O_3 dopant, as sintering temperature reached 1325 °C, the $Q \times f$ reached a maximum value of 27,506 (at 9.87 GHz). However, for V_2O_5 addition, the $Q \times f$ value showed increased slightly with rising the sintering temperature. According to SEM image, it is found that there are a number of needle-like secondary phase precipitated on grain boundaries as sintering temperature below 1325 °C. These secondary phases may degrade the quality factor. With increasing sintering temperature leads the crystalline grain more dense. The microwave dielectric loss is

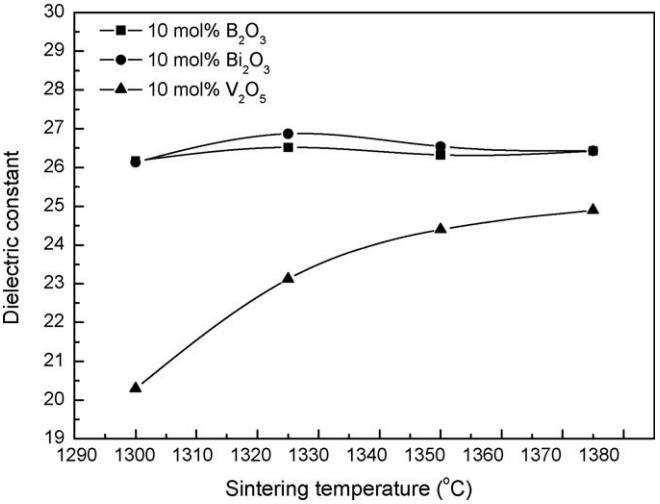

Fig. 6. The dependence of dielectric constant on sintering temperature for $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with 10 mol% B_2O_3, Bi_2O_3, and V_2O_5 additives.

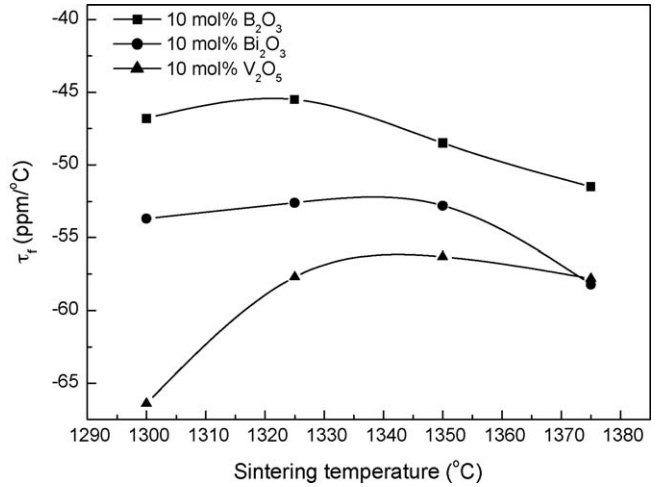

Fig. 8. The dependence of τ_f on sintering temperature for $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics with 10 mol% B_2O_3, Bi_2O_3, and V_2O_5 additives.

mainly caused not only by the lattice vibration modes, but also by the pores, second phases, impurities or even the lattice defect. 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 dependence of temperature coefficient of the resonant frequency (τ_f) of $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramics on sintering temperature with various sintering aids. All of the τ_f values drift toward positive τ_f at 1325 °C sintering temperature for 10 mol% of B_2O_3, Bi_2O_3, and V_2O_5 additions, the τ_f is −45.5 ppm/°C, −52.6 ppm/°C, and −57.8 ppm/°C, respectively, thereafter increase to negative τ_f.

4. Conclusion

The microwave dielectric properties of $Nd(Mg_{0.5}Ti_{0.5})O_3$ incorporated with different sintering aids, such as B_2O_3, Bi_2O_3, and V_2O_5 for lowering the sintering temperature were investigated. Comparing all this sintering aids, it is found that addition of 10 mol% B_2O_3 sintering at 1325 °C in $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramic can obtain the best microwave dielectric characteristics (dielectric constant (ε_r) = 26.2, $Q \times f$ = 61,307 GHz, and the temperature coefficient (τ_f) = −45.5 ppm/°C). Secondary phase was observed at 10 mol% V_2O_5 addition in the sintering temperature range of 1300–1325 °C, which leaded the degradation in microwave dielectric properties. The microwave dielectric properties as well as grain sizes, grain morphology, and bulk density were greatly dependent on sintering temperature and various sintering aids. The sintering temperature of $Nd(Mg_{0.5}Ti_{0.5})O_3$ microwave dielectric ceramics is generally high, about 1500 °C. Among these sintering aids, B_2O_3 may be suitable for applying in $Nd(Mg_{0.5}Ti_{0.5})O_3$ ceramic in this study. It can effectively lower sintering temperature about 175 °C from 1500 °C to 1325 °C. Therefore, this technique is useful to apply in the production of microwave communication devices, which requiring lower sintering temperature. The use of liquid-phase sintering, the liquid formed during firing normally remains as a grain boundary phase on cooling. This grain boundary phase can cause a deterioration of the microwave properties. Therefore, the selection of a suitable sintering aid is extremely important.

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