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New dielectric material system of $Nd(Mg_{1/2}Ti_{1/2})O_3$–$CaTiO_3$ with ZnO addition at microwave frequencies

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ABSTRACT

The microwave dielectric properties and the microstructures of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics prepared by the conventional solid-state route have been studied. Doping with 0.5 wt% ZnO can effectively promote the densification and the microwave dielectric properties of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$. The dielectric constant decreases from 145 to 30.5 as x varies from 0.1 to 1.0. In the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system, the microwave dielectric properties can be effectively controlled by varying the x value. The dielectric constant of 44, a $Q\times f$ value of 43,800 GHz and a τ_f value of 1.2 ppm/°C were obtained for $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C for 4 h. A band-pass filter is designed and simulated using the proposed dielectric to study its performance.

1. Introduction

The development of microwave communication systems requires materials which can be used as resonators in filters or oscillators at microwave frequencies in radar detectors, cellular telephones, and global positioning satellite (GPS) devices. To satisfy this demand, a material should have a reasonably high dielectric constant ($\varepsilon_r > 20$) to allow size reduction of the component, a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) in the microwave frequency range, and temperature stability ($\tau_f = 0$) [1]. The use of at least two compounds with negative and positive temperature coefficients, employed to form a solid solution or in mixed phases, is the most promising method for obtaining a zero τ_f. Although most dielectric ceramics with high dielectric constants have positive τ_f values, materials with a high dielectric constant, high Q and negative τ_f are desired to achieve this goal. Kim and colleagues have reported many complex perovskites $A(B_{1/2}{}^{2+}B_{1/2}{}^{4+})O_3$ with negative τ_f [2]. Among them, $Nd(Mg_{1/2}Ti_{1/2})O_3$ has a high dielectric constant ($\varepsilon \sim 27$), a high quality factor ($Q\times f$ value ~46,000 GHz) and a negative τ_f value (−49 ppm/°C). $CaTiO_3$ ($\varepsilon_r > 200$, $Q\times f < 1000$, $\tau_f > 1100$ ppm/°C) with a positive τ_f value was introduced into the mixture to form a solid solution $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ to compensate for the τ_f value.

Chemical processing and the use of small particles of starting materials normally reduce the sintering temperature of dielectric materials [3–6]. However, this requires a flexible procedure that increases the cost and time for fabrication of dielectric resonators. Liquid phase sintering by adding glass has been found to lower the firing temperature of ceramics. In this work, ZnO was selected as a sintering aid to lower the sintering temperature of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics.

2. Experimental procedure

Samples of $CaTiO_3$ and $Nd(Mg_{1/2}Ti_{1/2})O_3$ were individually synthesized by conventional solid-state methods from high-purity oxide (>99.9%) powders: $CaCO_3$, TiO_2, Nd_2O_3, and MgO. A small amount of ZnO (0.5 wt%) was added as a sintering aid. The starting materials were mixed according to the stoichiometry of $Nd(Mg_{1/2}Ti_{1/2})O_3$ and $CaTiO_3$, and then ground in distilled water for 10 h in a balling mill with agate balls. Both mixtures were dried and calcined at 1300 °C for 4 h. The crystalline phases of the calcined powder were identified by X-ray powder diffraction (XRD) analysis using Cu Kα radiation from 20° to 60° in 2θ. The calcined powder was mixed to the desired composition $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ and re-milled for 5 h with PVA solution as a binder. Pellets of 11 mm diameter and 5 mm thickness were uniaxially pressed. After debinding, the pellets were sintered at temperatures of 1325 °C for 4 h. The heating and cooling rates were both set at 10 °C/min.

The crystalline phases of calcined powder was identified by X-ray diffraction patterns. Microstructure observations of the sintered surface were made by scanning electron microscopy (SEM, Philips XL-40FEG). The bulk densities of the sintered pellets were measured using Archimedes method. The microwave dielectric properties were calculated from the sizes of the samples and the resonant frequency, using the Hakki and Coleman's dielectric resonant TE011 and TE01δ methods [7]. A HP8757D network analyzer and a HP8350 sweep oscillator were employed to make the measurements. The same technique was used to measure the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range of 25–80 °C. The temperature coefficient of resonant frequency (τ_f) was also measured by the same method associated using Eq. (1)

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

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where f_T is the resonant frequency of the dielectric resonator at temperature T (°C)

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns recorded for $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramic system sintered at 1325 °C for 4 h. It includes peaks that indicate the presence of $Nd(Mg_{1/2}Ti_{1/2})O_3$ and $CaTiO_3$ as crystalline phases. The mixed phases in the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramic system were formed because the structures were the same, and the solid solution system could be obtained. $CaTiO_3$ is a $GdFeO_3$-type perovskite structure and $Nd(Mg_{1/2}Ti_{1/2})O_3$ is also perovskite structure. All the peaks were indexed based on the perovskite unit cell. $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ solid solution exhibited a perovskite structure. The perovskite structure was identified without any second phase for all compositions tested in the experiment. However, non-linear variation with composition is clearly observed in the shift of XRD peak positions (Fig. 1). One can see that the compositions over x of 0.5 demonstrate a different variation in the peak shift, compared with the others ($x < 0.5$). Microwave dielectric properties ($Q \times f$ and τ_f) also show a non-linearity in this compositional range. Seabra et al. [8] investigated in detail the crystal structure (space group and cell parameter) of a solid solution formed in CT-LaMT, and related B-site ordering with the non-linear properties in the microwave dielectric properties. The symmetry changes when x is between 0.3 and 0.5 and is supported by the sudden change in the sign of τ_f values, dielectric properties and densities (see in Figs. 3–6).

The SEM micrographs of $(1-x)CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintering at 1325 °C for 4 h are illustrated in Fig. 2. The ceramics were already dense at 1325 °C. The grain growth was uniform and increased with x value. Because of $Nd(Mg_{1/2}Ti_{1/2})O_3$ have the lower sintering temperature.

The lattice parameters were calculated for different values of x from the X-ray diffraction patterns and the theoretical densities obtained using the lattice parameters are plotted in Fig. 3. Fig. 3 shows the observed variation of the bulk densities with composition. It is expected that the density should increase with increasing x because of the larger molecular weight of NMT. But the bulk density varies non-linearly in the region between $0.3 < x < 0.5$. The

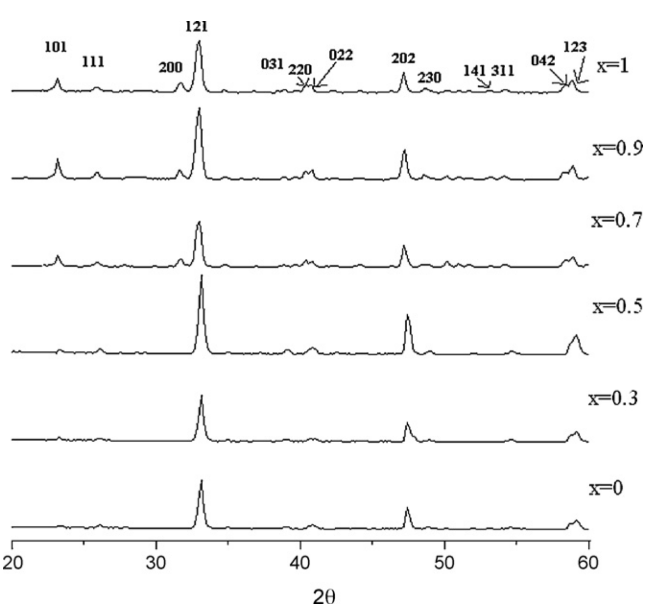

Fig. 1. X-ray diffraction patterns of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system with 0.5 wt% ZnO additive sintered at 1325 °C for 4 h.

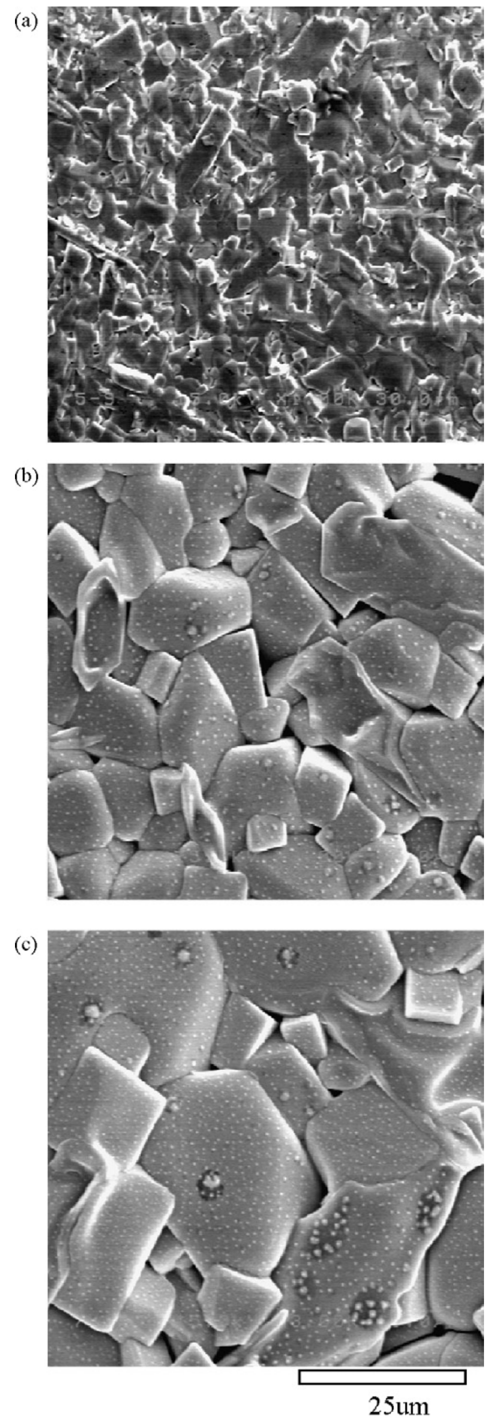

Fig. 2. SEM photographs of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintered at 1325 °C: (a) $x = 0.1$, (b) $x = 0.5$, and (c) $x = 0.9$.

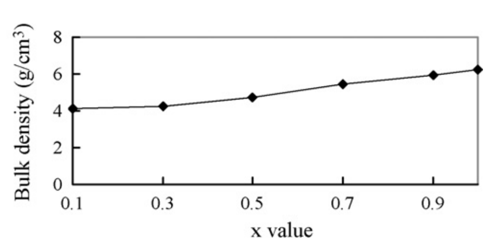

Fig. 3. Bulk density of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive system sintered at 1325 °C for 4 h.

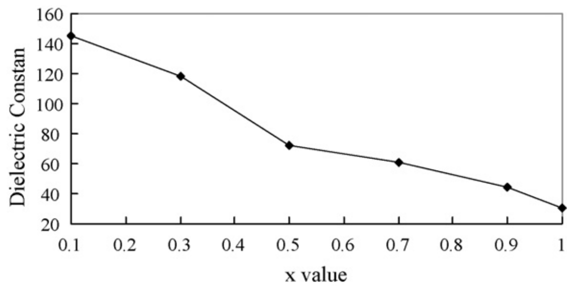

Fig. 4. Dielectric constant of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintered at 1325 °C for 4 h.

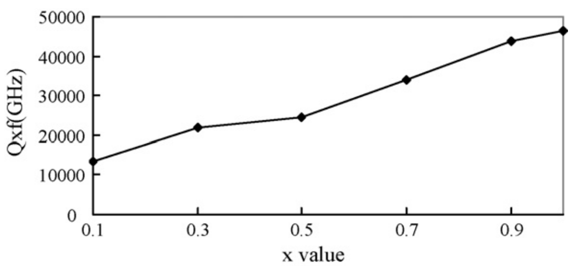

Fig. 5. $Q \times f$ value of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive system sintered at 1325 °C for 4 h.

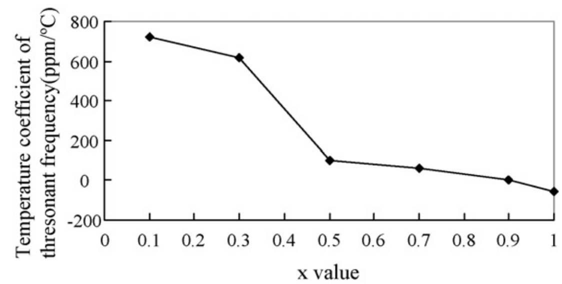

Fig. 6. Temperature coefficient of the resonant frequency of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintered at 1325 °C for 4 h.

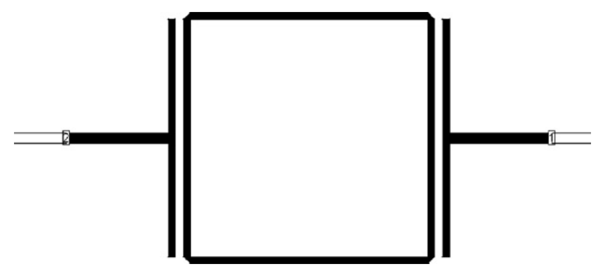

Fig. 7. Layout of slow-wave band-pass filter using ring resonators.

abrupt variation in the bulk density for the compositions with x between 0.3 and 0.5 is due to phase transformation as indicated by the microwave dielectric properties. Fig. 3 shows a plot of the density of the ZnO-doped $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics as a function of the x value. The figure reveals that densities of 4.2–6.24 g/cm^3 were obtained for $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics at sintering temperatures of 1325 °C. Density was also influenced by the composition and increased with x. The decrease in density as the sintering temperature increased was attributable to the pronounced grain boundary phases, indicating that increasing the $CaTiO_3$ content reduced the bulk density of the ceramics. But the bulk density varies non-linearly in the region $0.3 < x < 0.5$. The abrupt variation in the bulk density of the compositions with x between 0.3 and 0.5 is due to phase transformation as indicated by the microwave dielectric properties. Yeo et al. [9] have observed sharp variations in density for $(1-x)CaTiO_3 - xLa(Zn_{1/2}Ti_{1/2})O_3$ ceramics system. They have attributed the decrease in density to the numerous cracks and secondary phases. No such cracks or secondary phases were observed in the present system.

The permittivity of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintered at various temperatures for 4 h with different x value is shown in Fig. 4. The dielectric constant of $CaTiO_3$ and $Nd(Mg_{1/2}Ti_{1/2})O_3$ are 143 and 27, respectively. The permittivity decreased with increasing x value owing to a lower permittivity of $Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics. The dielectric constants decreased from 145 to 27 as the x value increased from 0.1 to 1. The relationship between ε_r values and sintering temperatures revealed the same trend with those between densities and sintering temperatures since higher density means lower porosity.

The factors that are believed to affect the microwave dielectric loss can be divided, such as the lattice vibrational 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. As shown in Fig. 5, the $Q \times f$ values of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with different x value sintered at 1325 °C, where the specimen possessed the highest density for the corresponding composition. The $Q \times f$ value increase with the increase of $Nd(Mg_{1/2}Ti_{1/2})O_3$ content. It was expected since that the quality factor of $Nd(Mg_{1/2}Ti_{1/2})O_3$ is much higher than that of $CaTiO_3$. But, the $Q \times f$ versus (x) plot shows a decrease in Q for composition in the range x between 0.3 and 0.5. This is attributed to the fact that the material undergoes a phase transition from *Pnma* space group to *Pmn*1 space group where the atoms are in a state of re-orientation to form the new structure. The maximum $Q \times f \sim$43,800 GHz for the investigated range ($0.1 \le x \le 1$) appeared at $x = 0.9$, where the specimen was sintered at 1325 °C for 4 h. It seems that the dielectric loss of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics system was dominated by the phase transformation.

In Fig. 6 shows the temperature coefficients of resonant frequency (τ_f) of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C. A τ_f value of 1.2 ppm/°C was obtained for $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% ZnO additive sintered at 1325 °C for 4 h. The temperature coefficient of the resonant frequency is well known to be governed by the composition, the additives and the second phase of the material. A higher $CaTiO_3$ content seemed to make the τ_f value more positive. The temperature coefficient of the resonant frequency was found to be related to the composition and the phase in ceramics. To verify the performance of the proposed material, a band-pass filter is designed for a center frequency of 2.4 GHz and fabricated on FR4, Al_2O_3 and $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$. Fig. 7 shows the physical layout of the designed filter with a center frequency of 2.4 GHz.

Table 1
Simulation results of the band-pass filters using different dielectrics.

Substrate	$\tan\delta$	ε_r	Size (mm^2)	Insertion loss (dB)	Return loss (dB)	f_o
FR4	0.015	4.5	19.87 × 18.3	1.8	15.8	2.39
Al_2O_3	0.003	9.8	9.13 × 8.12	0.87	21	2.4
$0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ with ZnO addition	0.0018	44	7.18 × 6.2	0.69	20	2.4

The simulation results are listed in Table 1. Compared to FR4 and alumina, the filter using the $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramic shows a tremendous reduction in the insertion loss and demonstrates a large reduction in its size. 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.

4. Conclusion

The dielectric characteristics of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with sintering aids ZnO were investigated. $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics exhibited perovskite structures. The $Q \times f$ varies non-linearly and increases for composition with $x \geqq 0.5$. The dielectric constant of 44, a $Q \times f$ value of 43,800 GHz and a τ_f value of 1.2 ppm/°C were obtained for $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C for 4 h. Compared to FR4 and alumina, the filter using $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics shows a tremendous reduction in the insertion loss and demonstrates a large reduction in its size.

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