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New dielectric material system of $Nd(Mg_{1/2}Ti_{1/2})O_3$–$CaTiO_3$ with V_2O_5 addition for microwave applications

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ABSTRACT

The effects of sintering aids additives on the microstructures and microwave dielectric properties of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics were investigated. The effects of V_2O_5 additions on the microwave dielectric properties and the microstructures of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics have been investigated. Doping with 0.5 wt% V_2O_5 can effectively promote the densification and the microwave dielectric properties of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$. It is found that $CaTiO_3$–$Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics can be sintered at 1325 °C due to the liquid phase effect of a V_2O_5 additions. The dielectric constant decreases from 140 to 28 as x varies from 0.1 to 1.0. The microwave dielectric properties indicate the possibility of a phase transformation for x between 0.3 and 0.5. A low-pass filter is designed and simulated using the proposed dielectric to study its performance.

1. Introduction

Rapid grow of the microwave communication system has stimulated a search for new effective low-cost materials for applications such as resonators and filters. The requirements for these materials are high dielectric permittivity (ε_r) and quality factor (Q) as well as a close to zero value of temperature coefficient of the resonant frequency (τ_f). Two or more compounds having negative and positive temperature coefficient values employed to form a solid solution or mixed phases are the most promising method to obtain zero temperature coefficient of resonant frequency.

Targeting at compensating their temperature coefficient of resonant frequency values, an effective method has been developed to combine two or more compounds with negative and positive temperature coefficients, respectively, to form solid solutions or mixed phases [1–3]. 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. Jong-Hee Kim et al. have reported many complex perovskites $A(B_{1/2}{}^{2+}B_{1/2}{}^{4+})O_3$ with negative τ_f [4]. 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 ~45,000 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 to into the mixture form a solid solution $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ to compensate for the τ_f value.

The main objective of this study was to investigate the sintering behavior and microwave dielectric properties of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ with the addition of 0.5 wt% V_2O_5 in order to lower the sintering temperature and improve the sinterability of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$. Added 0.5 wt% V_2O_5 as the sintering aids to lower the sintering temperature [5,6]. The relationships between the sintering temperatures, microstructure evolution and microwave dielectric properties of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ with various amounts of V_2O_5 are presented.

2. Experimental procedure

Samples of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ were prepared by conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of V_2O_5 (0.5 wt%) was added as a sintering aid. High purity oxide powders (>99.9%) $CaCO_3$, TiO_2, Nd_2O_3, and MgO were weighed and mixed for 24 h with distilled water. The starting materials were mixed according to the stoichiometry of $Nd(Mg_{1/2}Ti_{1/2})O_3$ and $CaTiO_3$, and ground in distilled water for 10 h in a baling 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 pressed by uniaxial pressing. After debinding, these pellets were sintered at temperatures of 1325 °C for 4 h. The heating and cooling rates were both set at 10 °C/min.

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The crystalline phases of calcined powder was identified by X-ray diffraction (XRD) patterns. The bulk densities of the sintered pellets were measured by the Archimedes method. The microwave dielectric properties were calculated from the sizes of the samples and the resonant frequency, using the Hakki and Colman's dielectric resonant TE011 and TE01δ methods [7]. A HP8757D network analyzer and a HP8350 sweep oscillator were employed to make the measurements. Identical 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 from +25 to +80 °C. The temperature coefficient of resonant frequency (τ_f) was also measured by the same method associated with calculate Eq. (1)

$$\tau_f\ (\text{ppm}/^\circ\text{C}) = \frac{f_{80} - f_{20}}{60 f_{20}} \times 10^6 \tag{1}$$

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

3. Results and discussion

X-ray diffraction patterns of 0.5 wt% V_2O_5 added $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C for 4 h are shown in Fig. 1. It includes peaks that indicate the presence of $Nd(Mg_{1/2}Ti_{1/2})O_3$ and $CaTiO_3$ as crystalline phases. The single phase of perovskite solid solution was clearly evidenced in the whole composition range.

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 [8] investigated in detail the crystal structure (space group and cell parameter) of a solid solution formed in $CaTiO_3$–$LaMg_{1/2}Ti_{1/2}$, and related B-site ordering with the non-linear properties in the microwave dielectric properties. $Nd(Mg_{1/2}Ti_{1/2})O_3$ composition arose from the 1:1 B-site ordering in a long range in $AB_1B_2O_3$ complex perovskite, where each Mg^{2+} surrounded by six Ti^{4+} neighbors and eachTi^{4+} surrounded by six Mg^{2+} neighbors altered in order, analogous to $La(Mg_{1/2}Ti_{1/2})O_3$ and $Ca(Al_{1/2}Nb_{1/2})O_3$ [9] perovskites. Therefore, the B-site LRO structure combined with the a-a-c+ tilting octahedral converted the crystal symmetry from the pseudo orthorhombic *Pbnm* space group into the resultant monoclinic $P2_{1/n}$ space group. Also, with the unit cell lattice parameters of $a = 5.489$ Å, $b = 5.5811$ Å, $c = 7.7681$ Å, and $\beta = 89.82°$, the XRD profile for $x = 1.0$ could be successfully indexed. Unit cell parameters in $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C shown in Table 1. Since the similar crystal symmetry between *Pbnm* and $P2_{1/n}$ space group except a neglectable distortion in angle β. Actually this increased anisotropic cell expansion could also be evidenced by the larger b/a length ratio in $Nd(Mg_{1/2}Ti_{1/2})O_3$ perovskite with $b/a = 1.015$ than that in $CaTiO_3$ perovskite of $b/a = 1.003$ [9].

Table 1
$(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ cell parameters.

x-Value	a (Å)	b (Å)	c (Å)	β	Space group
0.1	5.403	5.424	7.651	90	*Pbnm*
0.3	5.415	5.441	7.671	90	*Pbnm*
0.5	5.427	5.455	7.683	90	*Pbnm*
0.7	5.456	5.508	7.734	90	*Pbnm*
0.9	5.461	5.562	7.767	90	*Pbnm*

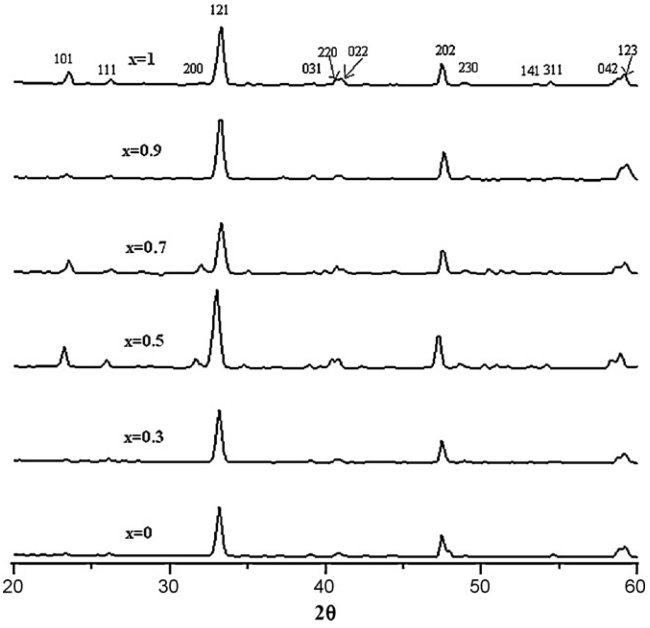

Fig. 1. X-ray diffraction patterns of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system with 0.5 wt% V_2O_5 additive sintered at 1325 °C for 4 h.

Fig. 2 shows the apparent densities of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1325 °C for 4 h. It is expected that the density should increase with increasing x because of the larger molecular weight of $Nd(Mg_{1/2}Ti_{1/2})O_3$. But the bulk density varies non-linearly in the region between $0.3 < x < 0.5$. The 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. 2 shows a plot of the density of the V_2O_5-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 4–6.1 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. has 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.

Fig. 3 shows the dielectric constants (ε_r) of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintering at 1325 °C for 4 h. 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 140 to 28 as the x

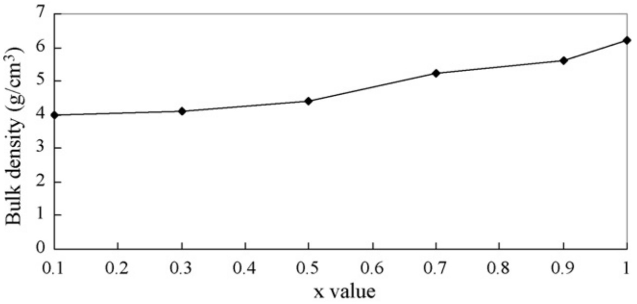

Fig. 2. Bulk density of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% V_2O_5 additive system sintered at 1325 °C for 4 h.

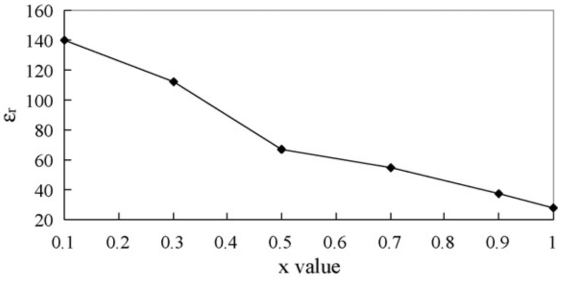

Fig. 3. Dielectric constant of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% V_2O_5 additive sintered at 1325 °C for 4 h.

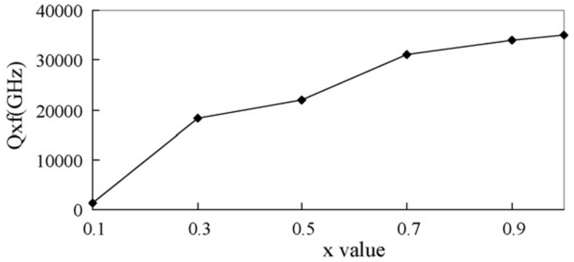

Fig. 4. $Q \times f$ value of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% V_2O_5 additive system sintered at 1325 °C for 4 h.

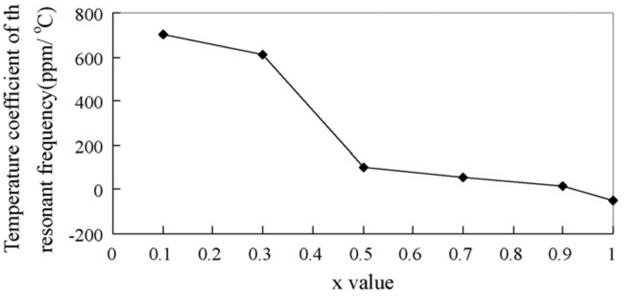

Fig. 5. Temperature coefficient of the resonant frequency of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% V_2O_5 additive sintered at 1325 °C for 4 h.

value increased from 0.1 to 1. The relationships 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 quality factor ($Q \times f$ values) of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintering at 1325 °C for 4 h is shown in Fig. 4. 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 $Q \times f \sim 34{,}100$ GHz for the investigated range ($0.1 \leq x \leq 1$) appeared at $x = 0.9$, where the specimen was sintered at 1325 °C for 4 h. Many factors could affect the microwave dielectric loss of dielectric resonators 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. 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.

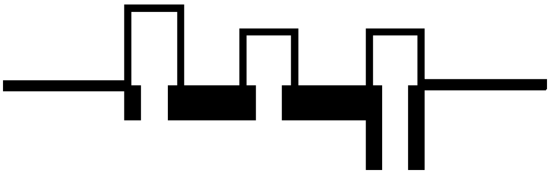

Fig. 6. Physical layout of the low-pass filter.

Table 2
Dimensions of the compact hairpin filter with different ceramic substrates.

	FR4	Alumina	$0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$
Dielectric constant (ε_r)	4.7	9.7	37
tan δ	0.015	0.0003	0.00034
Cutoff frequency (GHz)	1.98	1.96	2.01
Pass-band insertion loss (dB)	1	0.77	0.6
Pass-band return loss (dB)	10	11	16
Efficacious dimensions (mm^2)	28 × 18	18 × 10	14.75 × 4

Fig. 5 shows the temperature coefficients of resonant frequency (τ_f) of the $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintering at 1325 °C for 4 h. A τ_f value of 13.5 ppm/°C were obtained for $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% V_2O_5 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 low-pass filter is designed for a 3-dB cutoff frequency of 2 GHz and fabricated on FR4, Al_2O_3 and $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$. Fig. 6 shows the physical layout of the designed filter with a cutoff frequency of 2.0 GHz. The simulation results are listed in Table 2. 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.

4. Conclusions

The dielectric characteristics of $(1-x)CaTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with sintering aids V_2O_5 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 $x \geq 0.5$. The dielectric constant of 37, a $Q \times f$ value of 34,100 GHz and a τ_f value of 13.5 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. Therefore, the $0.1CaTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramic is suitable for applications in microwave dielectric resonators and filters because of its excellent microwave dielectric properties. 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.

References

[1] J. Zhang, J. Zhai, X. Chou, X. Yao, Solid State Commun. 147 (2008) 392–396.
[2] Y.-B. Chen, C.-L. Huang, S.-T. Tasi, Mater. Lett. 62 (2008) 2454–2457.
[3] K. Kageyama, J. Am. Ceram. Soc. 75 (1992) 1767.
[4] S.-Y. Cho, C.-H. Kim, D.-W. Kim, Mater. Res. Soc. 14 (1999) 2484.
[5] S.-Y. Cho, C.-H. Kim, D.-W. Kim, J. Mater. Res. 14 (1999) 2484–2487.
[6] Y.-B. Chen, C.-L. Huang, C.-W. Lo, Mater. Sci. Eng. B 128 (2006) 98–102.
[7] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Technol. 8 (1960) 402.
[8] M.P. Seabra, M. Avdeev, V.M. Ferreira, R.C. Pullar, N.Mc.N. Alford, J. Eur. Ceram. Soc. 23 (2003) 2403.
[9] M. Hu, H. Gu, X. Chu, J. Qian, Z. Xia, J. Appl. Phys. 104 (2008) 124104.