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New dielectric material system of $Nd(Mg_{1/2}Ti_{1/2})O_3$–$SrTiO_3$ in the microwave frequency range

Yuan-Bin Chen*

Department of Engineering & Management of Advanced Technology, Chang Jung Christian University, 396 Chang Jung Rd., Sec. 1, Kway Jen, Tainan 71101, Taiwan

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ABSTRACT

The microwave dielectric properties of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics prepared by the conventional solid state method have been investigated. Doping with 0.25 wt% B_2O_3 can effectively promote the densification and the microwave dielectric properties of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$. The dielectric constant decreases from 132 to 24 as x varies from 0.3 to 0.9. In the $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system, the microwave dielectric properties can be effectively controlled by varying the x value. At 1475 °C, $0.1SrTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ has a dielectric constant (ε_r) of 45.4, a $Q \times f$ value of 44,000 GHz and a temperature coefficient of resonant frequency (τ_f) of −3 ppm/°C.

1. Introduction

With the recent progress in microwave communication systems, microwave dielectric materials with a high quality factor, a good stability of the temperature coefficient of resonant frequency, and a high dielectric constant have been extensively studied because of their application to microwave devices such as filters, duplexers, voltage-controlled oscillators, and antennas. Present trends are the miniaturization of microwave devices and the narrowing of the channel bandwidth. To meet the demands of microwave circuit designs, each dielectric property must be precisely controlled [1–3].

Low-loss dielectric materials have played an important role in modern microwave telecommunication systems. Recently, the La-modified complex perovskites attracted a great attention as promising microwave dielectrics. One of the important characteristics of such materials is the temperature coefficient of resonant frequency (TCF), which should be as close to zero as possible for the successful application in thermally stable electronic devices. It was previously shown that $La(B'_{1/2}B''_{1/2})O_3$ perovskites presenting oxygen octahedral tilt and B'/B'' ordering have negative TCF while alkaline-earth-metal titanates have a positive one. Therefore, the preparation of solid solutions between those compositions is a promising way to obtain materials with TCF close to zero.

To satisfy the demands of microwave circuit designs, each dielectric property requires precise control. Using two or more compounds with negative and positive temperature coefficients to form a solid solution or mixed phases is the most promising method of obtaining a zero temperature coefficient of the resonant frequency, in our previous reports [4–6]. Many kinds of dielectric ceramics have been developed for microwave applications [7–11]. Several complex perovskites ceramics $A(B'_{1/2}B''_{1/2})O_3$ ($A = Me^{2+}, Me^{3+}$; $B' = Me^{2+}, Me^{3+}$; $B'' = Me^{4+}, Me^{5+}, Me^{6+}$) have been reported due to their excellent microwave dielectric properties [12–14,5,15]. 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) and perovskite structured strontium titanate ($SrTiO_3$: $\varepsilon r \sim 200$, $Q \times f$ value 1000 and τ_f value +1100 ppm/°C) with a positive τ_f value was introduced into the mixture to form a solid solution $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ to compensate for the τ_f value.

2. Experimental procedures

Samples of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ were prepared using conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. High purity oxide powders (>99.9%) $SrCO_3$, 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 $SrTiO_3$, and ground in distilled water for 10 h in a baling mill with agate balls. A small amount of B_2O_3 (0.25 wt%) was added as a sintering aid. 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 $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ 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 1475 °C for 4 h. The heating and cooling rates were both set at 10 °C/min.

The crystalline phases of calcined powder were identified by X-ray diffraction (XRD) patterns. Microstructure observations of the sintered surface were made by

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* Tel.: +886 6 3359815; fax: +886 6 335981.
E-mail address: cubnck@yahoo.com.tw

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scanning electron microscopy (SEM, Philips XL-40FEG). 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 [16]. 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 temperature coefficient of resonance frequency (τ_f) was measured in the temperature range of 25–80 °C using an invar cavity.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1450 °C for 4 h. The peaks were indexed assuming a $GdFeO_3$-type unit cell. $Nd(Mg_{1/2}Ti_{1/2})O_3$ was reported to have a monoclinic crystal structure ($P2_{1/n}$) with unit cell dimensions of $a = 5.498$ Å, $b = 5.581$ Å, and $c = 7.769$ Å. $SrTiO_3$ was reported to have a cubic crystal structure with cell dimension of $a = 3.90$ Å. The mixed phases in the $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramic system were formed because the structures were the same, and the solid solution system could be obtained. $SrTiO_3$ 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. $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ solid solution exhibited a perovskite structure. Fig. 1 shows the X-ray diffraction patterns of 0.25 wt% B_2O_3-doped $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics at 1450 °C. In Fig. 1, no secondary phases can be observed since detection of a minor phase by X-ray is extremely difficult. According to Chen [17], some weak peaks (marked by asterisk *) in Fig. 1 indicate the presence of in- or anti-phase octahedral tilting. There were no any other peaks of supercell reflection, such as

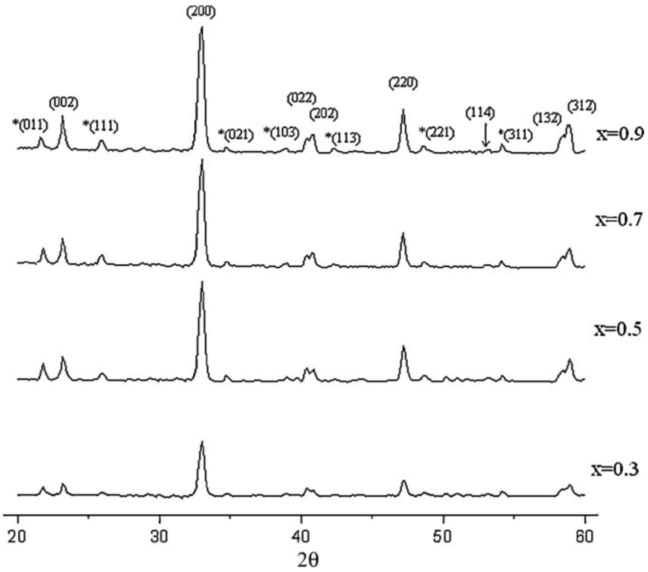

Fig. 1. X-ray diffraction patterns of the $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system additive sintered at various temperatures for 4 h.

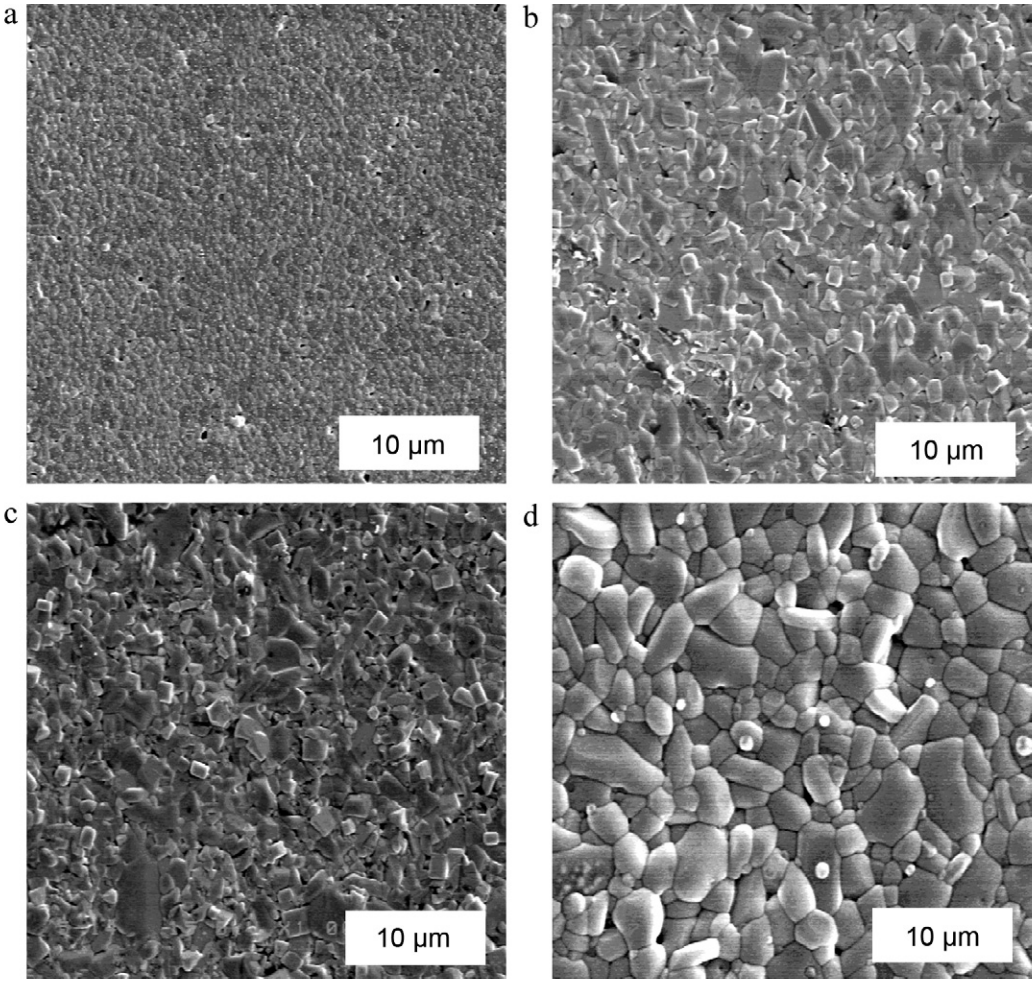

Fig. 2. SEM photographs of $0.1SrTiO_3$–$0.9xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at (a) 1300 °C, (b) 1325 °C, (c) 1350 °C, (d) 1375 °C, and (e) 1400 °C.

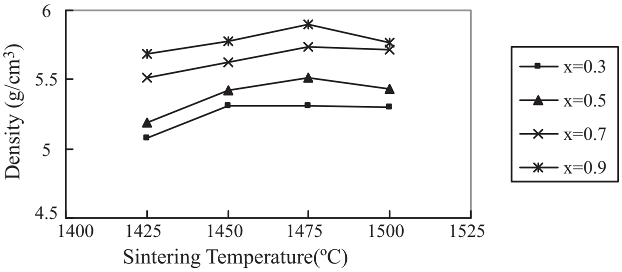

Fig. 3. Bulk density of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics system sintered at various temperatures for 4 h.

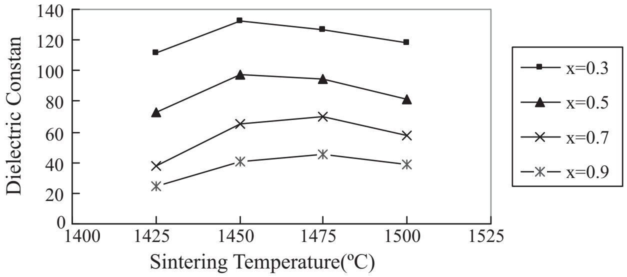

Fig. 4. Dielectric constant of the $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at various temperatures for 4 h.

Mg/Ti ordering, or antiparallel (Nd, Sr) displacement. The spectra were indexed according to an orthorhombic unit cell with space group *Pbnm* (no. 62, reference code: 01-089-5628 by PCPDF files). $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ system has an orthorhombic structure which is similar to the $CaTiO_3$–$L(Mg_{0.5}Ti_{0.5})O_3$ structure reported [18,19].

As can be seen in Table 1, a solid solution of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ was formed. $Nd(Mg_{1/2}Ti_{1/2})O_3$ (monoclinic, $P2_{1/n}$) and $SrTiO_3$ (cubic, *Pm*3*m*) perovskites were found to form solid solutions over the complete range. The $xNd(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)SrTiO_3$ $(0<x<1)$ solid solution system demonstrates gradual structural changes with increasing $SrTiO_3$ content [$P2_{1/n}$ (monoclinic) → *Pbnm* (orthorhombic) → *Imma* (orthorhombic) → *Pm*3*m* (cubic)], which are related to the loss of the B-site chemical ordering of $(x<0.1)$ displacement of the A-site cation $(x<0.3)$, in-phase tilting $(x<0.5)$, and one axis anti-phase tilting $(x<0.7)$, respectively [17]. In Table 1, the reduced cell volume gradually decreases with the increase of ST content. This means that although the average size of the A-site ions increases when the larger Sr^{2+} is introduced the total effect is determined by $(Mg, Ti)O_6$ octahedral contraction with the increase of smaller Ti^{4+} ion content. The evolution of the cell parameters is shown in Table 1.

In Fig. 2 the SEM micrographs of $0.1SrTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintering at various temperatures for 4 h are illustrated. The ceramics were already dense at 1475 °C. The grain growth increased with increasing sintering temperatures.

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. The figure reveals that densities of 5–6.01 (g/cm^3) were obtained for $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$. Density was also influenced by the composition and increased with x. The decrease of density with increasing sintering temperatures was due to the appearance of pores resulted from an inhomogeneous grain morphology as shown in Fig. 2.

The permittivity of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at various temperatures for 4 h with different x values is shown in Fig. 4. The dielectric constants of $SrTiO_3$ and $Nd(Mg_{1/2}Ti_{1/2})O_3$ are 200 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 132 to 24.6 as the x value increased from 0.3 to 0.9. 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.

As shown in Fig. 5, the $Q \times f$ values of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics with different x values sintered at various temperatures, where the specimen possessed the highest density for the corresponding composition. The $Q \times f$ value increases with the increase of $Nd(Mg_{1/2}Ti_{1/2})O_3$ content. It was expected since the quality factor of $Nd(Mg_{1/2}Ti_{1/2})O_3$ is much higher than that of $SrTiO_3$. 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 $Q \times f \sim 44{,}000$ GHz for the investigated range $(0.3 \le x \le 0.9)$ appeared at $x = 0.9$, where the specimen was sintered at 1475 °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 $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics system was dominated by the phase transformation.

Fig. 6 shows the temperature coefficients of the resonant frequency (τ_f) of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at various temperatures. A τ_f value of −3 ppm/°C was obtained for $0.1SrTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1475 °C for 4 h. The temperature coefficient of the resonant frequency is well known to be governed by the composition, the additives and the

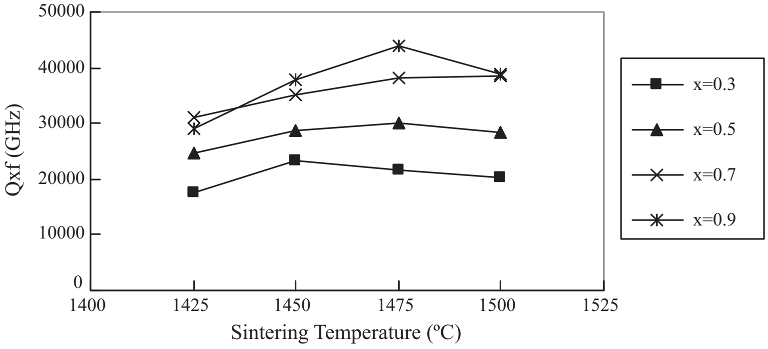

Fig. 5. $Q \times f$ value of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics system sintered at various temperatures for 4 h.

Table 1
$(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ cell parameters.

$(1-x)$ST–xNMT	a (Å)	b (Å)	c (Å)	Unit cell volume (Å^3)	Space group
NMT	5.4985	5.5812	7.7692	238.42298	$P2_{1/n}$
0.9NMT-0.1ST	5.4982	5.5801	7.7691	238.35991	*Pbnm*
0.7NMT-0.3ST	5.4981	5.5792	7.7687	238.29199	*Pbnm*
0.5NMT-0.5ST	5.4985	5.5755	7.7683	238.13053	*Pbnm*
0.3NMT-0.7ST	5.497	5.5724	7.7679	237.92521	*Imma*
0.1NMT-0.9ST	5.496	5.5713	7.7671	237.81474	*Imma*
ST	3.9	3.9	3.9	237.276	*Pm*3*m*

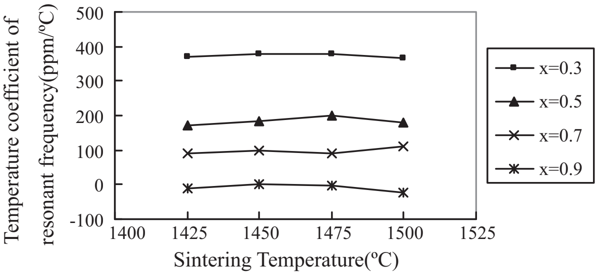

Fig. 6. Temperature coefficient of the resonant frequency of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at various temperatures for 4 h.

second phase of the material. Higher $SrTiO_3$ 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.

4. Conclusions

The dielectric properties of B_2O_3-doped $xNd(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)SrTiO_3$ ceramics were investigated. $Nd(Mg_{1/2}Ti_{1/2})O_3$ (monoclinic, $P2_{1/n}$) and $SrTiO_3$ (cubic, $Pm3m$) perovskites were found to form solid solutions over the entire range. The dielectric characteristics of $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics were investigated. $(1-x)SrTiO_3$–$xNd(Mg_{1/2}Ti_{1/2})O_3$ ceramics exhibited perovskite structures. The dielectric constant of 45.4, a $Q \times f$ value of 44,000(GHz) and a τ_f value of -3 ppm/°C were obtained for $0.1SrTiO_3$–$0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1475 °C for 4 h, which can be suitable candidate material for today's 3 G passive components and small-sized GPS patch antennas.

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