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Microwave dielectric properties of neodymium tin oxide

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Abstract

The microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics were investigated with a view to their application in mobile communication. $Nd_2Sn_2O_7$ ceramics were prepared by the conventional solid-state method with various sintering durations. A maximum density of 7.11 g/cm^3, a dielectric constant (ε_r) of 17.02, a quality factor (Qf) of 33,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of −55 ppm/°C were obtained when $Nd_2Sn_2O_7$ ceramics were sintered at 1550 °C for 9 h.

Keywords: $Nd_2Sn_2O_7$; Dielectric constant; Quality factor; Temperature coefficient of resonant frequency

1. Introduction

The advantages of using complex perovskite ceramics $A(B'_{0.5}B''_{0.5})O_3$ (A=Me^{2+}, Me^{3+}; B′=Me^{2+}, Me^{3+}; B″=Me^{4+}, Me^{5+}, Me^{6+}) are reportedly associated with their excellent microwave dielectric properties [1–3]. Extensive research into $Ln(Mg_{0.5}Ti_{0.5})O_3$ (Ln=La, Sm, Nd, Da, Y) ceramics and related ceramic systems have focused on their potential application in resonators, filters and antennas in modern communication systems, including radars and global positioning systems (GPS), which are operated at microwave frequencies [4,5]. $Ln(Mg_{0.5}Ti_{0.5})O_3$ ceramics exhibit a high dielectric constant (ε_r∼22–27), a high quality factor (Q∼3770–7550 at 10 GHz), and an adjustable temperature coefficient of resonant frequency.

Recently, numerous studies of $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics have been undertaken [6–10]. $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1550 °C for 4 h have been obtained with a dielectric constant of 19.3, a Qf of 43,300 GHz, and a τ_f of −57 ppm/°C. A dielectric constant of 18.9, a Qf of 32,300 GHz, and a τ_f of −52 ppm/°C were obtained for 0.25 wt% B_2O_3-doped $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics, sintered at 1500 °C for 4 h. A dielectric constant of 21.1, a Qf of 50,000 GHz, and a τ_f of −60 ppm/°C were obtained for $Nd(Mg_{0.5}Sn_{0.4}Ti_{0.1})O_3$ ceramics that were sintered at 1550 °C for 4 h. A dielectric constant of 19.2, a Qf of 68,900 GHz, and a τ_f of −67 ppm/°C were obtained for $Nd(Mg_{0.45}Co_{0.05}Sn_{0.5})O_3$ ceramics that were sintered at 1550 °C for 4 h. A dielectric constant of 19.5, a Qf of 129,200 GHz, and a τ_f of −66 ppm/°C were obtained when the $Nd(Mg_{0.4}Zn_{0.1}Sn_{0.5})O_3$ ceramics were sintered at 1500 °C for 4 h. The dielectric constant increased from 31.8 to 47.7, the Qf decreased from 54,200 to 42,800 GHz, and the τ_f increased from −43 to +41 ppm/°C as y increased from 0.5 to 0.7 when $(1-y)Nd(Mg_{0.4}Zn_{0.1}Sn_{0.5})O_3$–$yCa_{0.8}Sr_{0.2}TiO_3$ ceramic system sintered at 1600 °C for 4 h. A 0.5 wt% B_2O_3-doped $0.4Nd(Mg_{0.4}Zn_{0.1}Sn_{0.5})O_3$–$0.6Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system that was sintered at 1350 °C for 4 h had a dielectric constant of 38.3, a Qf of 35,000 GHz, and a τ_f of −4.8 ppm/°C.

Neodymium tin oxide ($Nd_2Sn_2O_7$) was found as a second phase in the composites [6–10]. The formation of this Sn-rich second phase was attributed to the loss of MgO upon ignition. However, no technical information on the microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics is available in the published literature. This fact motivates this investigation of the microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics. In this work, $Nd_2Sn_2O_7$ ceramics were synthesized using the conventional mixed-oxide method. The effects of the sintering duration on

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the microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics sintering at 1550 °C were explored. The microwave dielectric properties of the $Nd_2Sn_2O_7$ ceramics varied with the sintering duration. These microwave dielectric properties were further analyzed by densification, X-ray diffraction (XRD) patterns, and observation of their microstructures.

2. Experimental procedure

The $Nd_2Sn_2O_7$ ceramics were prepared by the conventional mixed-oxide method. The starting raw chemicals were Nd_2O_3 (99.99%) and SnO_2 (99.0%) powders. The raw materials were mixed in a manner consistent with the stoichiometric proportions of the $Nd_2Sn_2O_7$ ceramics. The powders were ball-milled in alcohol for 12 h and dried. The $Nd_2Sn_2O_7$ was then calcined at 1200 °C for 4 h. The calcined powder was re-milled for 12 h using PVA solution as a binder. The obtained powder was then crushed into fine particles and sieved through a 200 mesh. This very fine powder thus obtained was then axially pressed at 2000 kg/cm^2 into pellets with a diameter of 11 mm and a thickness of 6 mm. These pellets were then sintered at 1550 °C for 8–10 h in air. Both the heating rate and the cooling rate were set to 10 °C/min.

Following sintering, the phases of the samples were investigated by X-ray diffraction. An X-ray Rigaku D/MAX-2200 with Cu$K\alpha$ radiation (at 30 kV and 20 mA) was utilized along with a graphite monochromator in the 2θ range of 10–70°. Scanning electron microscopy (SEM; JEOL JSM-6500F) and energy dispersive X-ray spectrometry (EDS) were utilized to examine the microstructures of the specimens. Their apparent densities were measured by Archimedes' method in distilled water. The microwave dielectric properties of the specimens were measured using the postresonator method developed by Hakki and Coleman [11]. This scheme adopted a cylindrical specimen of diameter D and length L. The specimens whose microwave dielectric property was measured had an aspect ratio, D/L, of approximately 1.6, which is in the permitted range that was determined by Kobayashi and Katoh [12]. A cylindrical resonator was sandwiched between two conducting plates. Two small antennas were positioned close to the specimen to couple the microwave signal power into or out of the resonator. The other ends of the antennas were connected to an Agilent N5230A network analyzer. The resonance characteristics depended on the size and dielectric properties of the specimen. The microwave energy was coupled using electric-field probes. The TE_{011} resonant mode was optimal for obtaining the dielectric constant and the loss factor of the specimen. An Agilent N5230A network analyzer was utilized to identify the TE_{011} resonant frequency of the dielectric resonator, and the dielectric constant and quality factor were calculated. The value of τ_f was measured by the same method as the dielectric constant. The test cavity was placed in a chamber in which the temperature was increased from 25 to 75 °C. The τ_f value (ppm/°C) was determined from the change in resonant frequency,

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

where f_1 and f_2 are the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of the $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h. The X-ray diffraction patterns of $Nd_2Sn_2O_7$ ceramics did not vary significantly with sintering durations. The spectral angles of the X-ray diffraction peaks were the same following sintering at 1550 °C for 8–10 h.

Clearly, $Nd_2Sn_2O_7$ was the main crystalline phase, which was accompanied by small amount of Nd_2O_3 as the second phase. $Nd_2Sn_2O_7$ with a cubic crystal structure (ICDD-PDF #87-1220) and Nd_2O_3 with a hexagonal crystal structure (ICDD-PDF #74-1147) were identified.

Fig. 2 shows the microstructures of $Nd_2Sn_2O_7$ ceramics, following sintering at 1550 °C for 8–10 h. Comparing the microstructures of $Nd_2Sn_2O_7$ ceramics that were sintered for different durations indicated that the average grain size increased with the sintering duration. To identify the composition of the second phase, an energy-disperse spectroscopy (EDS) analysis was carried out on the grains of the $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h, as shown in Fig. 2(b). The quantitative analysis, presented in Table 1, reveals that grains A and B were $Nd_2Sn_2O_7$ and the grain C was Nd_2O_3.

Fig. 3 displays the amounts of the main phase and apparent densities of the $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 8–10 h. The amount of the main phase was evaluated from strongest lines of both main and second phases,

$$Nd_2Sn_2O_7\ (vol\%) = \frac{I_{A(2\,2\,2)}}{I_{A(2\,2\,2)} + I_{B(0\,1\,1)}} 100 \quad (2)$$

where I_A and I_B are the strongest lines of $Nd_2Sn_2O_7$ (2 2 2) and Nd_2O_3 (0 1 1), respectively. The amount of the main phase sintering at 1550 °C remained stable as sintering duration increased from 8 to 9 h and increased from 87.31% to 89.77% as sintering duration increased from 9 to 10 h. The formation of the second phase of Nd_2O_3 affected the apparent density and microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics. The apparent densities of the $Nd_2Sn_2O_7$ ceramics sintered at

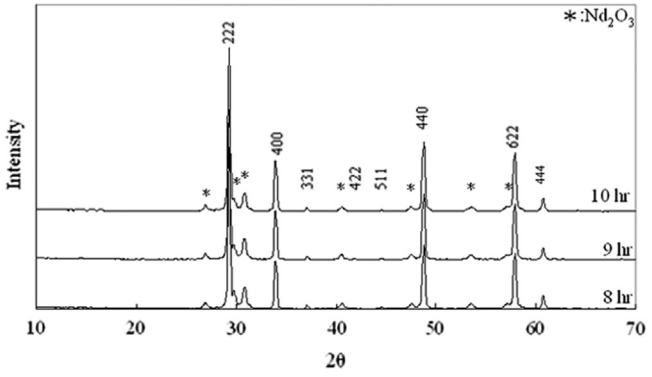

Fig. 1. X-ray diffraction patterns of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h.

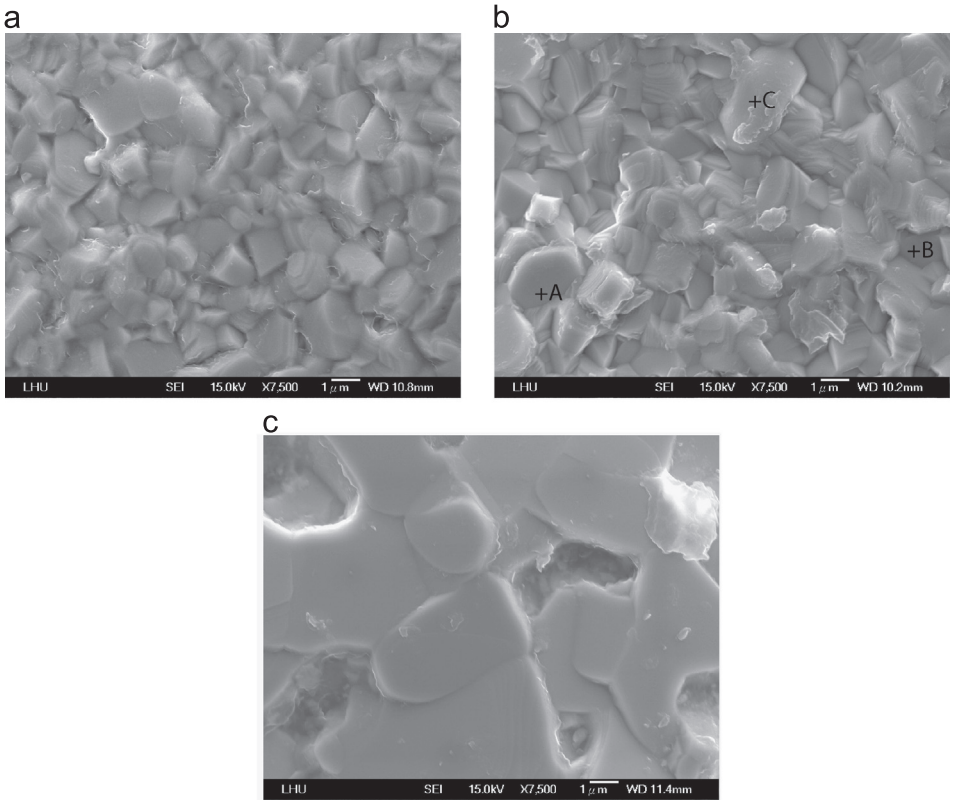

Fig. 2. Microstructures of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h: (a) 8 h, (b) 9 h, and (c) 10 h.

Table 1
EDS data of grains of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 9 h.

Atomic element	Nd (%)	Sn (%)	O (%)
A	13.62	12.92	73.46
B	14.23	13.13	72.64
C	32.84	0	67.16

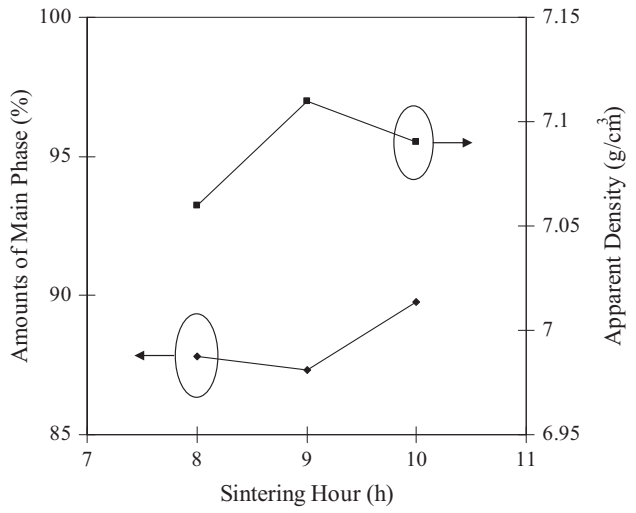

Fig. 3. Amounts of main phase and apparent densities of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h.

1550 °C was highest when the sintering duration was performed for 9 h, beyond which sintering duration it declined. The density of the composites can be calculated by following equation:

$$D_{composite} = V_1 D_1 + V_2 D_2, \quad (3)$$

where $D_{composite}$ is the density of the composite, V_1 and V_2 are the volume fractions of $Nd_2Sn_2O_7$ and Nd_2O_3, respectively, and D_1 and D_2 are the densities of $Nd_2Sn_2O_7$ and Nd_2O_3, respectively. The theoretical densities of $Nd_2Sn_2O_7$ and Nd_2O_3 are 7.18 and 7.24 g/cm^3, respectively. Since the amount of the Nd_2O_3 ceramics was highest when the sintering duration was performed for 9 h, the apparent density of the composites is inferred to be highest.

Fig. 4 displays the relative densities and dielectric constants of the $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 8–10 h. $Nd_2Sn_2O_7$ ceramic that was sintered at 1550 °C for 9 h had the highest relative density of 98.92%. The dielectric constant of $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C ranged from 16.9 to 17.0 as the sintering time varied from 8 to 10 h. $Nd_2Sn_2O_7$ ceramic that was sintered at 1550 °C for 9 h had the highest dielectric constant of 17.0. Many factors, including the second phase and relative density, affect the dielectric constant of $Nd_2Sn_2O_7$ ceramic. The dielectric constant of the composites can be calculated using the mixture rule,

$$\ln \varepsilon_r = v_1 \ln \varepsilon_{r1} + v_2 \ln \varepsilon_{r2} \quad (4)$$

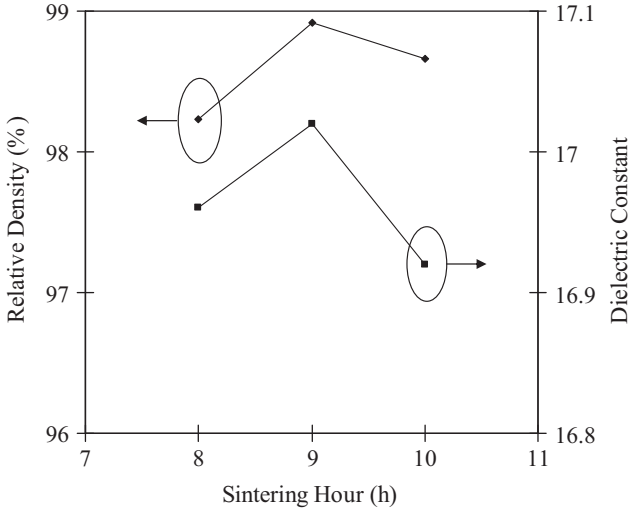

Fig. 4. Relative densities and dielectric constants of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h.

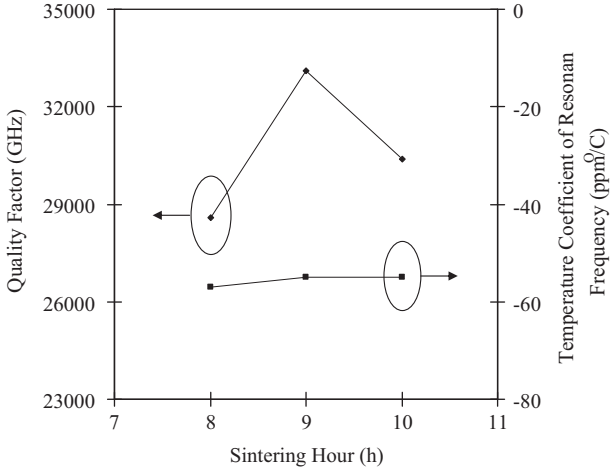

Fig. 5. *Qf* and temperature coefficient of resonant frequency (τ_f) of $Nd_2Sn_2O_7$ ceramics sintered at 1550 °C for 8–10 h.

where ε_r is the dielectric constant of the composite, v_1 and v_2 are the volume fraction of $Nd_2Sn_2O_7$ and Nd_2O_3, respectively, and ε_{r1} and ε_{r2} are the dielectric constants of $Nd_2Sn_2O_7$ and Nd_2O_3, respectively. The overall dielectric constant is inferred to increase with the amount of the second phase. A dielectric constant of 17–18 was obtained for Nd_2O_3 [13]. Since the dielectric constant of Nd_2O_3 was almost the same as that of $Nd_2Sn_2O_7$ ceramic, the effect of the second phase Nd_2O_3 could be neglected. The variation in the dielectric constant in the $Nd_2Sn_2O_7$ ceramics was associated with the relative density. A higher relative density is associated with a lower porosity and, therefore, with a higher dielectric constant.

Fig. 5 presents the *Qf* and temperature coefficient of resonant frequency (τ_f) of the $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 8–10 h. $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h had the highest *Qf* of 33,100 GHz. Many factors govern the microwave dielectric loss, which is composed of intrinsic and extrinsic losses. Intrinsic loss is associated with the lattice vibrational modes. Extrinsic loss is determined by the density, porosity, second phases, impurities, oxygen vacancies, grain size and lattice defects [14,15]. Nd_2O_3 ceramics had a *Q* of 222, which is smaller than that of $Nd_2Sn_2O_7$ [16]. $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h contained the most second phase; it was inferred to have the lowest *Qf*. However, the *Qf* of $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h was highest, owing to relative density. Since the *Qf* of $Nd_2Sn_2O_7$ ceramics was consistent with the variation of the relative density, the *Qf* of $Nd_2Sn_2O_7$ ceramics is believed to be dominated by the relative density. Generally, τ_f is related to the composition, the amount of additive, and the secondary phases that are present in ceramics. The τ_f of $Nd_2Sn_2O_7$ ceramics ranged from −57 to −55 ppm/°C as the sintering conditions varied. No significant variation in the τ_f of the $Nd_2Sn_2O_7$ ceramics with sintering duration was observed. $Nd_2Sn_2O_7$ ceramic that was sintered at 1550 °C for 9 h had a τ_f of −55 ppm/°C. The relatively high τ_f of the $Nd_2Sn_2O_7$ ceramics precludes its immediate application in resonator device. A later investigation will involve preparing of the specimen by combining two compounds with negative and positive temperature coefficients.

4. Conclusions

The effects of sintering duration on the microwave dielectric properties of $Nd_2Sn_2O_7$ ceramics were examined. $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h had a relative density of 98.92%, a dielectric constant of 17.02, and a *Qf* of 33,100 GHz. The relative density dominated the dielectric constant and *Qf* of $Nd_2Sn_2O_7$. $Nd_2Sn_2O_7$ ceramics that were sintered at 1550 °C for 9 h had a temperature coefficient of resonant frequency (τ_f) of −55 ppm/°C. $Nd_2Sn_2O_7$ ceramics have a lower dielectric constant and *Qf* than these properties of $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics. It indicates the existence of $Nd_2Sn_2O_7$ phase in a media of low dielectric constant which acts as a loss dielectric inside dense $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics. $Nd_2Sn_2O_7$ ceramics have less negative τ_f than that of $Nd(Mg_{0.5}Sn_{0.5})O_3$ ceramics, implying that the presence of the $Nd_2Sn_2O_7$ phase shifts the τ_f of the specimen in the positive direction.

Acknowledgments

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