Effect of sintering temperature and time on microwave dielectric properties of Nd$_2$WO$_6$ ceramics

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The microwave dielectric properties of Nd$_2$WO$_6$ ceramics were investigated with a view to their application in mobile communication. Nd$_2$WO$_6$ ceramics were prepared by the conventional solid-state method with various sintering temperatures and sintering times. A maximum density of 7.45 g/cm$^3$ and an open porosity of 2.1% were obtained for Nd$_2$WO$_6$ ceramic, sintered at 1500°C for 4 h. A dielectric constant ($\varepsilon_r$) of 15.6, a quality factor ($Q\times f$) of 50,600 GHz, and a temperature coefficient of resonant frequency ($\tau_f$) of $-65$ ppm/°C were obtained when Nd$_2$WO$_6$ ceramics that were sintered at 1500°C for 4 h.

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1. Introduction

The demand for novel microwave ceramics application has been increasing rapidly in the mobile communication industries during the last decade. Numerous investigations have focused on developing good microwave dielectric materials to achieve device miniaturization and system stability. Materials that are to be used in microwave devices must have three dielectric characteristics—a high dielectric constant, a high quality factor, and a near-zero temperature coefficient of resonant frequency. These enable small devices with low loss and high temperature stability, respectively, to be fabricated. According to previous studies, R$_2$MoO$_4$ ceramics exhibit three polymorphs, with monoclinic, cubic, and tetragonal symmetries, depending on the synthesis conditions. A $\varepsilon_r$ of 15.4, a $Q\times f$ of 19,200 GHz, and a $\tau_f$ of $-59$ ppm/°C were obtained when Nd$_2$MoO$_6$ ceramics that were sintered at 1350°C for 4 h.

Recent investigations show that the dielectric properties of microwave ceramics are dependent on their constituent ions. A $\varepsilon_r$ of 10.8 and a $Q\times f$ of 76,990 GHz were obtained for CaMoO$_4$ ceramics that were sintered at 1000°C for 3 h. A $\varepsilon_r$ of 10.4 and a $Q\times f$ of 76,550 GHz were obtained for CaWO$_4$ ceramics that were sintered at 1100°C for 3 h. BaMoO$_4$ ceramics sintered at 800°C for 3 h possessed a $\varepsilon_r$ of 9.2 and a $Q\times f$ of 26,580 GHz. BaWO$_4$ ceramics sintered at 850°C for 3 h possessed a $\varepsilon_r$ of 8.2 and a $Q\times f$ of 21,120 GHz. Replacing the Mo$^{6+}$ in Nd$_2$MoO$_6$ ceramics by W$^{6+}$ ions can substantially affect sintering behavior and dielectric properties of microwave ceramics. This phenomenon motivates this investigation of the effect of the substitution of Mo$^{6+}$ by W$^{6+}$ to form Nd$_2$WO$_6$ ceramics.

In this paper, Nd$_2$WO$_6$ ceramics were synthesized herein using the conventional mixed-oxide method. The effects of the sintering temperature and the sintering time on the microwave dielectric properties of Nd$_2$WO$_6$ ceramics were explored. The dielectric properties of Nd$_2$WO$_6$ ceramics at microwave frequencies were found to vary with the sintering temperature and sintering time. For further understanding of these different microwave dielectric properties, they were analyzed by densification, X-ray diffraction (XRD), and microstructural observations.

2. Experimental procedure

Nd$_2$O$_3$ (99.9%) and WO$_3$ (99.8%) were used as the starting raw materials. The compound Nd$_2$WO$_6$ were prepared by the conventional mixed-oxide method. The raw materials were weighed out in stoichiometric proportions, ball-milled in alcohol, dried, and 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 a fine powder through a sieve with a 200 mesh. The obtained fine powder was then axially pressed at 2000 kg/cm$^2$ into pellets with a diameter of 11 mm and a thickness of 6 mm. The specimens thus obtained were then sintered at temperatures of 1400 to 1550°C for 4 h and at 1500°C for 2–6 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 data was used with Cu K$_\alpha$ radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 10–80°. The selected area electron diffraction patterns of the specimen were examined using transmission electron microscopy (TEM; JEOL JEM 2100). Scanning electron microscopy (SEM; JEOL JSM-6500F) was utilized to elucidate the microstructures of the specimens. The apparent densities of which were measured using the Archimedes method with distilled water as the liquid. The microwave dielectric properties of the specimens were measured using the postresonator method of developed by Hakki and Coleman. The postresonator scheme adopted a specimen in the form of a cylinder of diameter $D$ and length $L$. The specimens used for making microwave dielectric property measurements had an aspect ratio $D/L$ of approximately 1.6, which is in the range permitted by Kobayashi and Katoh. The scheme for measuring $\tau_f$ was the same as that for measuring the dielectric constant.

3. Results and discussion

Figure 1 displays the X-ray diffraction patterns of Nd$_2$WO$_6$ ceramics that were sintered at different temperatures for 4 h. Clearly, Nd$_2$WO$_6$ is the main crystalline phase. The crystal
structure of Nd$_2$WO$_6$ has monoclinic structure belongs to $I2/a$ space group. As evidenced by Fig. 1, the spectral angles of the X-ray diffraction peaks were the same following sintering at different temperatures for 4 h. The X-ray diffraction patterns of Nd$_2$WO$_6$ ceramics did not significantly vary with sintering temperature. Figure 2 shows the selected area electron diffraction pattern (SAED) of Nd$_2$WO$_6$ ceramics that were sintered at 1500°C for 4 h. The SAED pattern was composed of concentric rings of bright spots. The SAED pattern shows the character of polycrystalline. Electron beam diffracts from the crystallographic planes of the unit cells composing the specimen.

Figure 3 shows the microstructures of Nd$_2$WO$_6$ ceramics under various sintering conditions. The presences of cracks were observed in the SEM photographs of the samples which were sintered at temperatures of 1400°C for 4 h. As the sintering temperature increased from 1400 to 1500°C, the pores were eliminated and densification occurred. The pores of Nd$_2$WO$_6$ ceramics almost disappeared upon sintering at 1500°C for 4 h. The pores and cracks may influence the microdielectric properties of Nd$_2$WO$_6$ ceramics. Comparing the microstructures of Nd$_2$WO$_6$ ceramics sintered under various conditions revealed that the grain size increased with the sintering temperature and sintering time.

Table 1 shows the average grain size of the specimens under various sintering conditions. The average grain size of Nd$_2$WO$_6$ ceramics increased from 0.75 to 3.86 μm as the temperature of sintering for 4 h increased from 1400 to 1550°C. The average grain size of Nd$_2$WO$_6$ ceramics that were sintered at 1500°C increased from 1.33 to 3.83 μm as the sintering temperature varied from 2 to 6 h. An energy-disperse spectroscopy (EDS) analysis was carried out on the grains of Nd$_2$WO$_6$ ceramics that were sintered at 1500°C for 4 h, as shown in Fig. 3(c). The quantitative analysis, presented in Table 2, reveals that grains A and B are Nd$_2$MoO$_6$.

Table 1 shows the open porosity of the specimens under various sintering conditions. The open porosity of Nd$_2$WO$_6$ ceramics decreased dramatically from 8.1 to 3.3% as the temperature of sintering for 4 h increased from 1400 to 1450°C. The open porosity of Nd$_2$WO$_6$ ceramics were lower than 2.4% and spanned in the range from 2.0 to 2.4%, following sintering at 1550°C for 2–6 h.

Figures 4 and 5 display the apparent densities and dielectric constants of the Nd$_2$WO$_6$ ceramics that were sintered at 1400–1550°C for 4 h and at 1500°C for 2–6 h, respectively. The apparent density of Nd$_2$WO$_6$ ceramics that were sintered at 1400–1550°C for 4 h was highest when sintering was conducted at 1500°C, beyond which temperature, it declined. Furthermore, the apparent densities of Nd$_2$WO$_6$ ceramics sintered at 1500°C increased with sintering time to a maximum at 4 h, and thereafter decreased. The apparent density did not increase significantly with the sintering time, implying that the apparent density was not enhanced by increasing the sintering time but mainly determined by the sintering temperature. Nd$_2$WO$_6$ ceramics that were sintered at 1500°C for 4 h had a maximum apparent density of 7.45 g/cm$^3$. The increase in apparent density may be caused by the decrease in the number of pores, as presented in Fig. 3. The $\varepsilon_r$ of Nd$_2$WO$_6$ ceramics increased from 13.7 to 15.6 as the temperature of sintering for 4 h increased from 1400 to 1500°C. It fell from 15.6 to 15.5 as the sintering temperature increased from 1500 to 1550°C for 4 h. The $\varepsilon_r$ of Nd$_2$WO$_6$ ceramics that were sintered at 1500°C ranged from 15.3 to 15.6 as the sintering time varied from 2 to 6 h. The apparent density is extrinsic factor in controlling the dielectric constant. The $\varepsilon_r$ of Nd$_2$WO$_6$ ceramics was similar to the variation of the apparent density. The $\varepsilon_r$ of Nd$_2$WO$_6$ ceramics is suggested to be dominated by the apparent density.

Figure 6 shows the corrected dielectric constants of Nd$_2$WO$_6$ ceramics that were sintered at different temperatures for 4 h. The corrected dielectric constants of Nd$_2$WO$_6$ ceramics can be calculated by following equation:

$$\varepsilon_{\text{measured}} = \varepsilon_{\text{corrected}} \left[ 1 - \frac{3P(\varepsilon_{\text{corrected}} - 1)}{2\varepsilon_{\text{corrected}} + 1} \right].$$

(1)

where $\varepsilon_{\text{corrected}}$ and $\varepsilon_{\text{measured}}$ is the corrected and measured dielectric constants of the composite, respectively, and $P$ is the fractional porosity. The corrected dielectric constants of Nd$_2$WO$_6$ ceramics were in the range from 16.5 to 16.9 as sintering temperature varied from 1400 to 1550°C. No significant variation in corrected dielectric constant of Nd$_2$WO$_6$ ceramics with sintering temperature over the entire range of sintering temperatures considered herein was observed. The $\varepsilon_r$ of Nd$_2$WO$_6$ ceramic can be calculated using the Clausius-Mossotti equation, as suggested by Tohdo et al.:

$$\varepsilon_{\text{correct}} = \frac{3V_m + 8\pi\alpha_0}{3V_m - 4\pi\alpha_0}.$$

(2)

where $V_m$ is the molar volume, and $\alpha_0$ is the sum of ionic polarizabilities of individual ions. The calculated $\varepsilon_{\text{correct}}$ of Nd$_2$WO$_6$ ceramics is 17.9, using Eq. (2). The $\varepsilon_{\text{correct}}$ is close to the calculated one. Nd$_2$WO$_6$ ceramics have a higher $\varepsilon_r$ than that of Nd$_2$MoO$_6$ ceramics, as expected. This fact may be explained by the ionic polarization. As revealed by Eq. (2), the $\varepsilon_r$ increases with the ionic polarization. The polarization of the W$^{6+}$ ion is
Table 1. Average grain size and open porosity of Nd$_2$WO$_6$ ceramics that were sintered at 1400–1550°C for 4 h and at 1500°C for 2–6 h.

| Sintering temperature (°C) | Sintering time (h) | Average grain size (μm) | Open porosity (%) |
|---------------------------|-------------------|-------------------------|-------------------|
| 1400                      | 4                 | 0.75                    | 8.1               |
| 1450                      | 4                 | 1.34                    | 3.3               |
| 1500                      | 2                 | 1.33                    | 2.0               |
|                            | 4                 | 2.14                    | 2.1               |
|                            | 6                 | 3.83                    | 2.4               |
|                            | 4                 | 3.86                    | 2.7               |

Table 2. EDS data of grains of Nd$_2$WO$_6$ ceramics sintered at 1400°C for 4 h.

| Atomic element | Nd (%) | W (%) | O (%) |
|----------------|--------|-------|-------|
| A              | 24.08  | 14.70 | 61.22 |
| B              | 22.29  | 14.92 | 62.79 |

Fig. 3. Microstructures of Nd$_2$WO$_6$ ceramics sintered under various sintering conditions.

Fig. 4. Apparent densities and dielectric constant of Nd$_2$WO$_6$ ceramics sintered at 1400–1550°C for 4 h.
higher than that of Mo$^{6+}$ ion$^{11,12}$, so the εr of the Nd$_2$WO$_6$ ceramics is higher than that of Nd$_2$MoO$_6$ ceramics.

Figures 7 and 8 present the Q×f and $\tau_f$ of Nd$_2$WO$_6$ ceramics that were sintered at 1400–1550°C for 4 h and 1500°C for 2–6 h, respectively. The Q×f of Nd$_2$WO$_6$ ceramics increased from 19,800 to 50,600 GHz as the temperature of sintering for 4 h increased from 1400 to 1500°C. However, it decreased from 50,600 to 47,000 GHz as the temperature of sintering for 4 h increased from 1500 to 1550°C. The Q×f of Nd$_2$WO$_6$ ceramics that were sintered at 1500°C increased from 26,100 to 50,600 GHz as the sintering time increased from 2 to 4 h, and decreased from 50,600 to 22,400 GHz as the sintering time increased from 4 to 6 h. The relationship between the Q×f and the sintering temperature was similar to that between the apparent density and the sintering temperature, because the microwave dielectric loss is affected by several factors, and consists of intrinsic and extrinsic components. Intrinsic loss is associated with the lattice vibrational modes. Extrinsic loss is related to the density, porosity, second phases, impurities, oxygen vacancies, grain size, and lattice defects.$^{13,14}$ Since the Q×f of Nd$_2$WO$_6$ ceramics was similar to the variation of the apparent density, the Q×f of Nd$_2$WO$_6$ ceramics is suggested to be dominated by the apparent density. The Q×f of Nd$_2$WO$_6$ ceramics is higher than that of Nd$_2$MoO$_6$ ceramics was associated with the packing fraction. The packing fraction can be calculated using the following equation:

\[
\text{Packing fraction} (\%) = \frac{\text{volume of packed ions}}{\text{volume of unit cell}} \times z \tag{3}
\]

where z is the number of formula units per unit cell. For Nd$_2$WO$_6$ and Nd$_2$MoO$_6$ ceramics have packing fractions of 69.81 and 68.79%, respectively. The packing fraction of Nd$_2$WO$_6$ ceramic is higher than that of Nd$_2$MoO$_6$ ceramic. The $\tau_f$ of Nd$_2$WO$_6$ ceramics decreased from −54 to −65 ppm/°C as the temperature of sintering for 4 h increased from 1400 to 1500°C, and spanned in the range from −65 to −64 ppm/°C, following sintering at 1500–1550°C for 4 h. The $\tau_f$ of Nd$_2$WO$_6$ ceramics were −65 ppm/°C, following sintering at 1500°C for 2–6 h. Generally, $\tau_f$ is related to the composition, the amount of additive, and the second phases that are present in ceramics. The $\tau_f$ of Nd$_2$WO$_6$ ceramic shifted to zero as the sintering temperature decreased from 1500 to 1400°C. This is associated with the fact that the temperature coefficient of the resonant frequency can be expressed by the sum of temperature coefficient of the dielectric constant and the coefficient of thermal expansion.$^{15}$ The dielectric constant of
Nd$_2$WO$_6$ ceramics decreased significantly as the sintering temperature decreased from 1500 to 1400°C and, therefore, the absolute value of $\alpha_1$ and $\tau_e$ decreased. A $\alpha_1$ of $-65$ ppm/°C was measured for Nd$_2$WO$_6$ ceramic that was sintered at 1500°C for 4 h. The $\tau_e$ values of Nd$_2$MoO$_6$ ceramics that were sintered at 1350°C for 4 h was $-59$ ppm/°C.$^5$ It became more negative when Mo$^{6+}$ ions were replaced by W$^{6+}$ ions. This is associated with the fact that the temperature coefficient of the resonant frequency can be expressed by the sum of temperature coefficient of the dielectric constant and the coefficient of thermal expansion. The $\tau_e$ can be calculated by:

$$\tau_e = -\alpha_1 - \frac{1}{2} \tau_r,$$

(4)

where $\alpha_1$ is the coefficient of thermal expansion and $\tau_r$ is the temperature coefficient of dielectric constant. The temperature coefficient of dielectric constant ($\tau_r$) can be calculated by,$^{15}$

$$\tau_r = \frac{1}{\varepsilon} \left( \frac{\partial\varepsilon}{\partial T} \right)_p = \left( \frac{\varepsilon - 1}{\varepsilon} \right) \frac{(\varepsilon - 1)(\varepsilon + 2)}{\varepsilon} (A + B + C)$$

(5)

where $A = \frac{1}{3\varepsilon} \left( \frac{\partial\varepsilon_m}{\partial T} \right)_p$, $B = \frac{1}{3\varepsilon_m} \left( \frac{\partial\varepsilon_m}{\partial T} \right)_p$, $C = \frac{1}{3\varepsilon_m} \left( \frac{\partial\varepsilon_m}{\partial T} \right)_p$.

The temperature coefficient of dielectric constant ($\tau_r$) depended on dielectric constant. The dielectric constant of Nd$_2$WO$_6$ ceramics was higher than that of Nd$_2$MoO$_6$ ceramics and, therefore, the absolute value of $\tau_e$ and $\tau_r$ of Nd$_2$WO$_6$ ceramics was higher than that of Nd$_2$MoO$_6$ ceramics.

4. Conclusions

The effects of sintering temperature and sintering time on the microwave dielectric properties of Nd$_2$WO$_6$ ceramics were examined. The dielectric constant and $Q\times f$ of Nd$_2$WO$_6$ ceramics were mainly determined by the apparent density. The dielectric constant and $Q\times f$ of Nd$_2$WO$_6$ ceramics were higher than that of Nd$_2$MoO$_6$ ceramics, thus the dielectric constant and $Q\times f$ of Nd$_2$WO$_6$ ceramics were improved by substituting Mo$^{6+}$ ions with W$^{6+}$ ions.

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References

1) Y. B. Chen, J. Ceram. Soc. Japan, 123, 374–377 (2015).
2) Y. B. Chen, J. Ceram. Soc. Japan, 122, 708–713 (2014).
3) Y. B. Chen, J. Ceram. Soc. Japan, 122, 955–958 (2014).
4) F. De Smet, M. Devillers, C. Poleunis and P. Bertrand, J. Chem. Soc., Faraday Trans., 94, 941–947 (1998).
5) F. De Smet, P. Ruiz, B. Delmon and M. Devillers, J. Phys. Chem. B, 105, 12355–12363 (2001).
6) Y. C. Chen and M. Z. Weng, J. Mater. Sci.: Mater. Electron., 26, 853–859 (2015).
7) E. S. Kim, B. S. Chun, R. Freer and R. J. Cernik, J. Eur. Ceram. Soc., 30, 1731–1736 (2010).
8) B. W. Hakki and P. D. Coleman, IRE. Trans. Microwave Theory Tech., 8, 402–410 (1960).
9) Y. Kobayashi and M. Katoh, IEEE Trans. Microwave Theory Tech., 33, 586–592 (1985).
10) Y. Tohdo, K. Kakimoto, H. Ohsato, H. Yamada and T. Okawa, J. Phys. Chem. B, 109, 5399–5439 (2005).
11) J. R. Shannon, J. Appl. Phys., 73, 348–366 (1993).
12) C. Veneis, P. K. Davies, T. Negus and S. Bell, Mater. Res. Bull., 31, 413–437 (1996).
13) B. D. Silverman, Phys. Rev., 125, 1921–1930 (1962).
14) W. S. Kim, T. H. Hong, E. S. Kim and K. H. Yoon, Jpn. J. Appl. Phys., 37, 3567–3571 (1998).
15) A. J. Bosman and E. E. Havinga, Phys. Rev., 129, 1593–1600 (1963).