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Synthesis and properties of TiO_2 added $NiNb_2O_6$ microwave dielectric ceramics using a simple process

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Abstract

TiO_2 added $NiNb_2O_6$ ceramics produced using a reaction-sintering process were investigated. Pure columbite $NiNb_2O_6$ could be obtained without TiO_2 addition. With 30 and 40 mol% TiO_2 addition, a phase with the same structure of $Ni_{0.5}Ti_{0.5}NbO_4$ formed. Grain growth is easier in pellets with 30 and 40 mol% TiO_2 addition than in the $NiNb_2O_6$ pellets. Microwave dielectric properties: $\varepsilon_r = 20.7$, $Q \times f = 19{,}800$ GHz (at 9 GHz) and $\tau_f = -31.9$ ppm/°C were obtained for $NiNb_2O_6$ pellets sintered at 1300 °C/2 h. ε_r around 45, $Q \times f = 5400$–7700 GHz (at 6 GHz) and $\tau_f \sim 73$ ppm/°C were obtained in pellets with 30 mol% TiO_2 addition. ε_r around 50, $Q \times f = 3800$–5700 GHz (at 6 GHz) and $\tau_f \sim 99$ ppm/°C were obtained in pellets with 40 mol% TiO_2 addition.

Keywords: Powders-solid state reaction; Sintering; Dielectric properties; Niobates; TiO_2

1. Introduction

Microwave dielectric ceramics have been widely investigated for use as resonators and filters in satellite and mobile communication systems.[1,2] $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ complex perovskite compounds were reported to exhibit excellent microwave dielectric properties.[3,4] However, a very high sintering temperature is needed to obtain these complex perovskite ceramics. Besides, Ta_2O_5 is expensive as compared with Nb_2O_5. The columbite niobate compounds MNb_2O_6 (where M = Mg, Zn, Ni, Ca, Cu, Mn, and Co) have received much attention due to their low sintering temperature and low cost.[5–8] $ZnNb_2O_6$ (ZN) ceramics were reported to exhibit dielectric properties: $\varepsilon_r = 25$, $Q \times f = 83{,}700$ GHz, and $\tau_f = -56.1$ ppm/°C. For the $NiNb_2O_6$ (NN) ceramics, $\varepsilon_r \sim 22.6$, $Q \times f \sim 40{,}100$ GHz, and $\tau_f \sim -38$ ppm/°C were reported.[6] Therefore, these materials have been investigated for the applications in microwave dielectric resonators. TiO_2 ceramics were found with $\varepsilon_r = 100$, $Q \times f = 48{,}000$ GHz, and $\tau_f = +420$ ppm/°C.[9] It is possible to obtain $(1-x)ZnNb_2O_6$–$xTiO_2$ ceramics with $\tau_f \sim 0$ ppm/°C. Kim et al. investigated $(1-x)ZnNb_2O_6$–$xTiO_2$ ceramics and found $\tau_f \sim 0$ ppm/°C at $x = 0.58$.[10] As the magnitude of τ_f for NN is lower than ZN, it is suggested that $(1-x)NiNb_2O_6$–$xTiO_2$ ceramics with $\tau_f \sim 0$ ppm/°C could be obtained at $x < 0.58$.

Recently, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics produced via a simple and effective reaction-sintering process were reported by Liou and Tseng.[11] These have been the first successful synthesis of perovskite relaxor ferroelectric ceramics without the calcinations step in the traditional oxide route involved. PMN ceramics with a high density 8.09 g/cm^3 (99.5% of the theoretical value) and high dielectric constant 19,900 (1 kHz) were obtained. This reaction-sintering process had also been used to produce other complex perovskite relaxor ceramics. In recent studies, we also prepared $BaTi_4O_9$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, and $CaNb_2O_6$ (CN) ceramics using this process.[12–14] Microwave dielectric properties: $\varepsilon_r = 14.66$, $Q \times f = 22{,}300$ GHz, and $\tau_f = -22.6$ ppm/°C could be obtained in CN ceramics.[14] In this study, we try to obtain $NiNb_2O_6$

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columbite ceramics and $(1-x)NiNb_2O_6$–$xTiO_2$ with $x = 0.3$ and 0.4 using the reaction-sintering process.

2. Experimental procedures

All samples in this study were prepared from reagent-grade oxides: NiO (99.8%, SHOWA, Japan), Nb_2O_5 (99.8%, High Purity Chemicals, Japan), and TiO_2 (99.9%, SHOWA, Japan). Appropriate amounts of raw materials for NN and $(1-x)NiNb_2O_6$–$xTiO_2$ ($x = 0.3$ and 0.4; NT3 and NT4) were weighted and milled for 12 h in acetone with zirconia balls. After the slurry was dried and pulverized, the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick (6–7 mm thick for microwave properties measurement). The pellets were then heated at a rate 10 °C/min and sintered in a covered alumina crucible at temperatures ranging from 1200 to 1350 °C for 2 h in air.

We analyzed the sintered pellets using X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analyzed using scanning electron microscopy (SEM). The density of the sintered pellets was measured using the Archimedes method. The dielectric constants (ε_r) at microwave frequency (at 9 GHz for NN and at 6 GHz for NT3 and NT4) were calculated based on the sizes of the samples and the frequency of the TE_{011} mode using the Hakki–Coleman dielectric resonator method.[15] Temperature coefficient of resonant frequency (τ_f) at microwave frequency was measured in the temperature range from 25 to 85 °C, and calculated using the following equation:

$$\tau_f\,(\mathrm{ppm}/^\circ\mathrm{C}) = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6$$

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively. An Agile3nt N5230A network analyzer was used to measure the frequencies.

3. Results and discussions

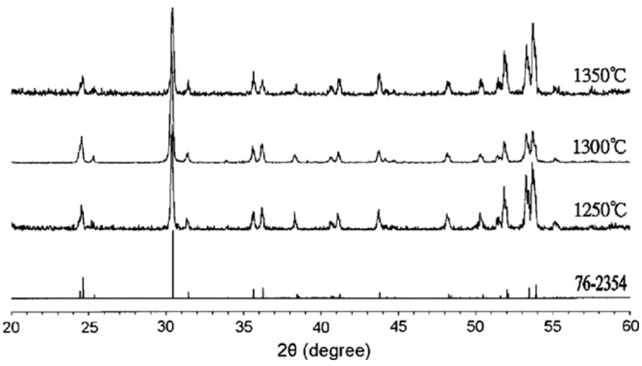

Fig. 1. XRD patterns of NN ceramics sintered at 1250–1350 °C for 2 h.

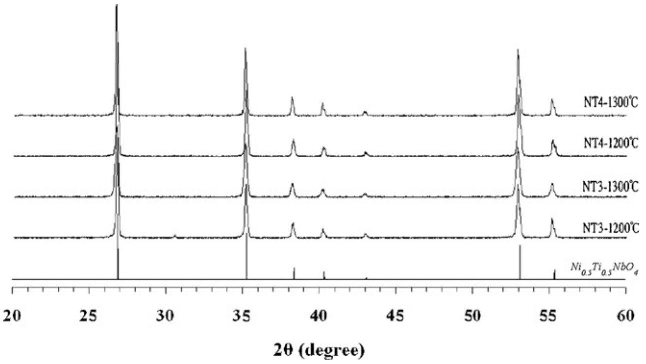

Fig. 2. XRD patterns of NT3 and NT4 ceramics sintered at 1200–1300 °C for 2 h.

The XRD profiles of NN ceramics sintered at 1250–1350 °C for 2 h are shown in Fig. 1. The reflections match well with those of $NiNb_2O_6$ in JCPD file no. 76-2354. This proves that columbite phase $NiNb_2O_6$ ceramics could be obtained via the reaction-sintering process with the calcinations bypassed. This simple process is effective not only in preparing $BaTi_4O_9$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $CaNb_2O_6$, and Pb-based complex perovskite ceramics but also effective in preparing $NiNb_2O_6$ ceramics. Phases with the same structure of $Ni_{0.5}Ti_{0.5}NbO_4$ (ICDD PDF# 00-052-1875) formed in the sintered NT3 and NT4 ceramics as shown in Fig. 2. This means the formation of $Ni_{0.5}Ti_{0.5}NbO_4$ phase is easier than the formation of $NiNb_2O_6$ phase when TiO_2 was added into the mixture of NiO and Nb_2O_5. In $M^{2+}M^{4+}Nb_2O_8$ (M^{2+} = Be, Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd; M^{4+} = Ti, Zr, Ge, Sn) investigated by Baumgarte and Blachnik, solid solutions based on the rutile structure ($a = 4.6968(2)$ Å and $c = 3.0238(2)$ Å)

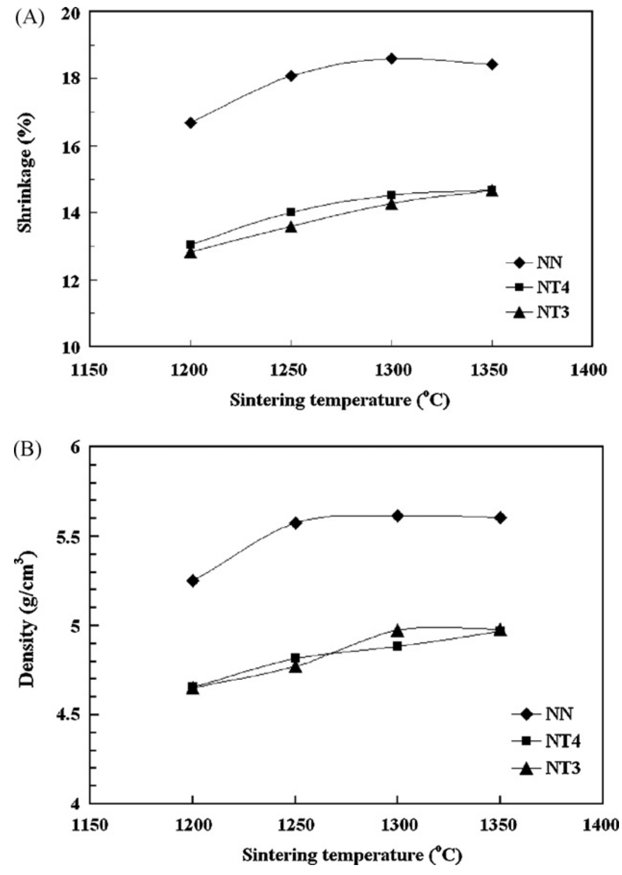

Fig. 3. Shrinkage percentages (A) and density (B) of NN, NT3, and NT4 ceramics sintered at various temperatures and soak time.

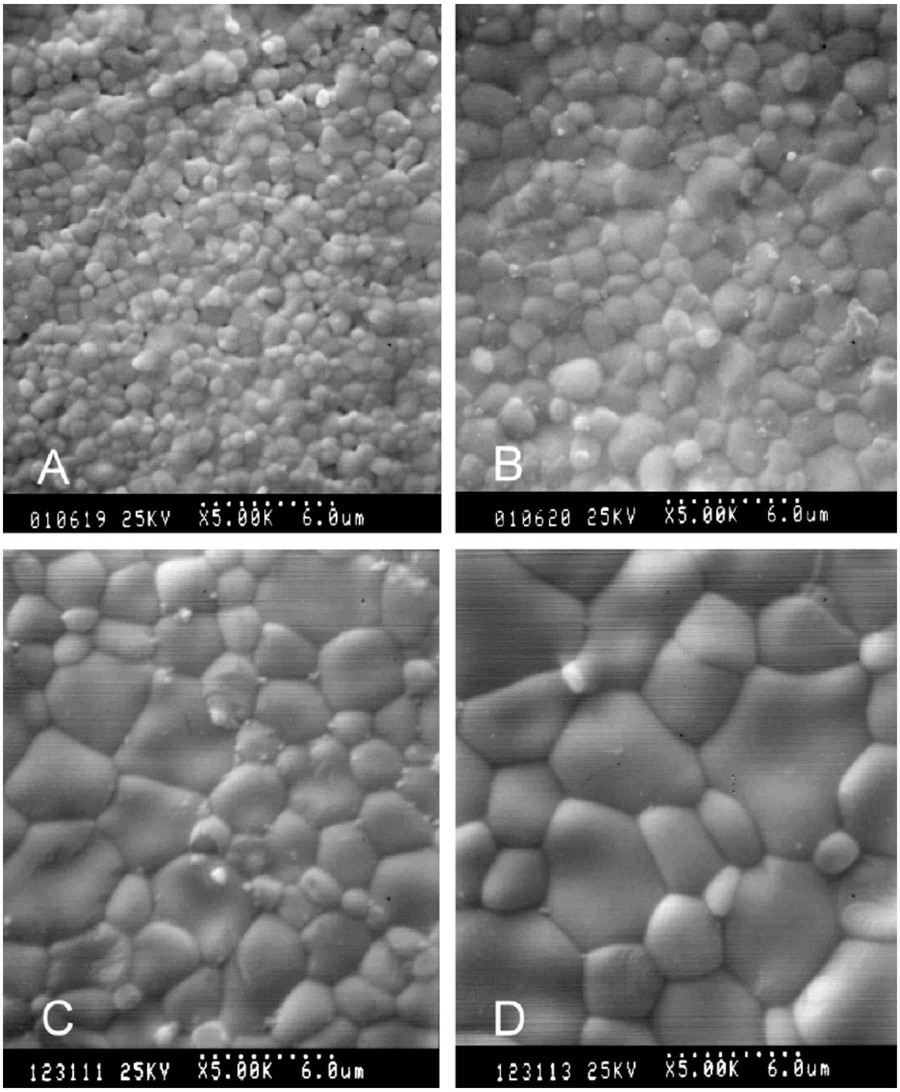

Fig. 4. SEM photographs of as-fired NN ceramics sintered at (A) 1200 °C, (B) 1250 °C, (C) 1300 °C, and (D) 1350 °C for 2 h.

appear in $NiTiNb_2O_8$ after being calcined at 1200 °C/48 h and sintered at 1200 °C/44 h. The α-PbO_2-related ixiolite structure ($a = 4.6746(5)$ Å, $b = 5.6621(5)$ Å, and $c = 5.0137(4)$ Å) appeared in $ZnTiNb_2O_8$.[16] In $(1-x)ZnNb_2O_6$–$xTiO_2$, Kim et al. observed four phase regions with increasing TiO_2 content. A solid solution based on the columbite structure was observed up to ~50 mol% TiO_2. At higher TiO_2 content only the ixiolite phase $ZnTiNb_2O_8$ appeared. Between 57 and 60 mol% TiO_2, a narrow mixture region of ixiolite and rutile was observed. There is a morphotropic phase transition for this composition region.[17] The fourth solid solution region between 60 and 100 mol% TiO_2 exhibited a rutile structure.[10] The morphotropic phase transition of columbite $NiNb_2O_6$ to $Ni_{0.5}Ti_{0.5}NbO_4$ phase for $(1-x)NiNb_2O_6$–$xTiO_2$ occurred at a lower TiO_2 content <30 mol% as shown in Fig. 2.

The shrinkage percentage and density of NN, NT3, and NT4 pellets are shown in Fig. 3. Lower shrinkage percentage and density values are observed in NT3 and NT4 pellets. The sintering temperature for a full densification in NN is 1250 °C. Higher sintering temperatures are needed to obtain dense NT3 and NT4 pellets. In our previous work, we found the shrinkage percentage increased from ~13% at 1330 °C sintering to 18–19% at 1400–1450 °C sintering and saturated at 1370 °C sintering in CN ceramics via reaction-sintering process.[14] In $MgNb_2O_6$ (MN), the shrinkage percentage saturated at 1250 °C sintering and 18.3% was observed after sintering at 1250 °C for 2 and 4 h. In ZN, the shrinkage percentage saturated at 1100 °C and 19–20% was found after sintering at 1200 °C.[18] In this study, 120 °C lowered sintering temperature is needed in NN as compared with CN. Maximum density 5.62 g/cm^3 (99.8% of theoretical value) for NN is found at 1300 °C/2 h sintering as shown in Fig. 3. Pullar et al. reported NN ceramics with a density around 96% of theoretical value was found after calcining at 1000 °C and sintering at 1250 °C via traditional oxide route.[19] In CN ceramics, a maximum 4.37 g/cm^3 (92% of the theoretical value) was found at 1420 °C/2 h sintering.[14] In ZN and MN prepared via reaction-sintering process, 98.7% and 97.1% of the theoretical density was obtained, respectively.[18] It is easier to obtain highly dense pellets in NN than in CN, ZN, and MN via the reaction-sintering process. Maximum density for NT3 and NT4 is obtained at

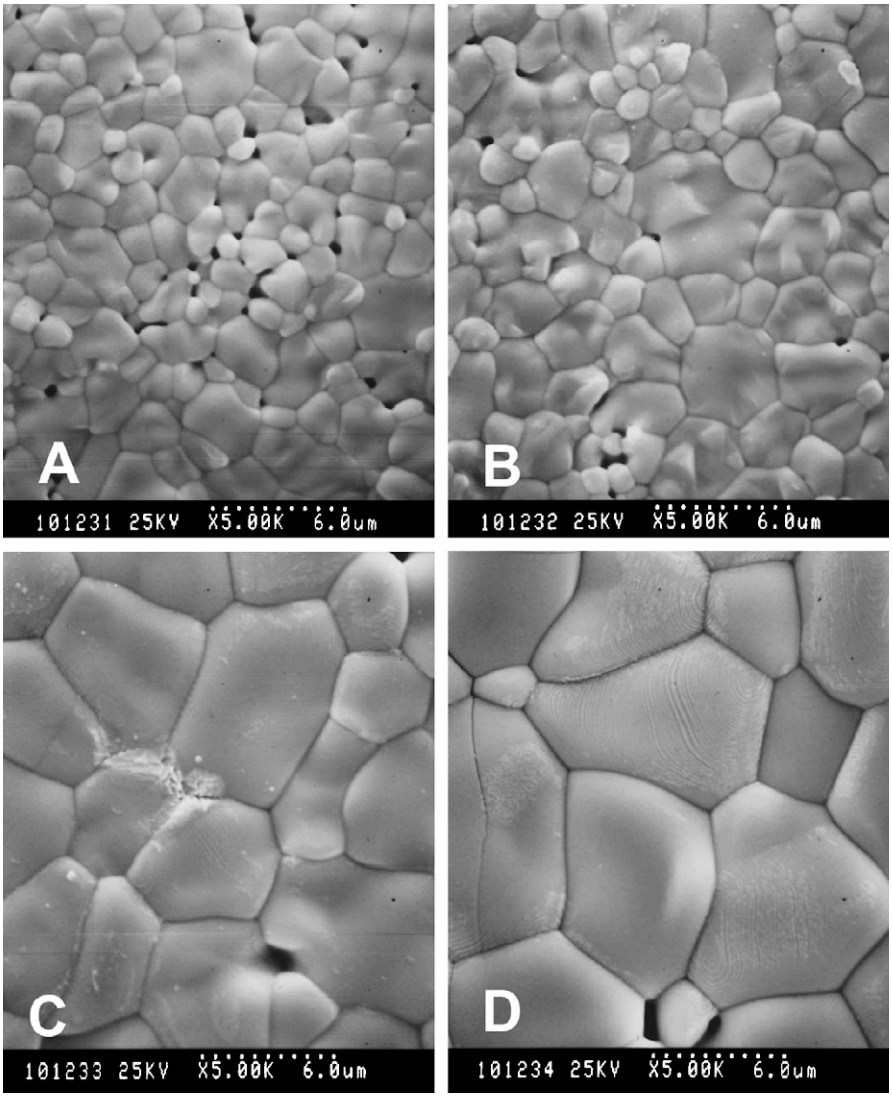

Fig. 5. SEM photographs of as-fired NT3 ceramics sintered at (A) 1200 °C, (B) 1250 °C, (C) 1300 °C, and (D) 1350 °C for 2 h.

1350 °C/2 h sintering and is found to be 4.98 g/cm^3 (95% of theoretical value of $\mathrm{Ni_{0.5}Ti_{0.5}NbO_4}$, 5.24 g/cm^3) and 4.97 g/cm^3 (94.8% of theoretical value of $\mathrm{Ni_{0.5}Ti_{0.5}NbO_4}$, 5.24 g/cm^3), respectively.

In Fig. 4, grains less than 1 μm were observed in NN pellets sintered at 1200 °C/2 h indicating 1200 °C was not high enough for the grain growth. Pores disappeared and grain size increased significantly in NN pellets sintered at temperatures above 1250 °C. This is in consistent with the shrinkage percentage in Fig. 3. The SEM photos of the as-fired NT3 and NT4 pellets are shown in Figs. 5 and 6. Larger grains were found indicating the grain growth in these pellets is easier than in the NN pellets. The grain sizes of NN, NT3, and NT4 pellets are shown in Fig. 7. 1–5 μm grains were seen in NN pellets and 2.4–6.8 μm grains were seen in NT3 and NT4 pellets. As compared with MN and ZN prepared via reaction-sintering process, grain growth is more difficult in NN than in MN and ZN. 0.4–4.2 μm grains were formed in MN pellets sintered at 1150–1300 °C for 2 and 4 h. In ZN pellets, 0.9–6.9 μm grains were formed after sintered at 1100–1250 °C for 2 and 4 h.[18]

Dielectric constant of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h are shown in Fig. 8. A low value 14.3 is found in NN pellets sintered at 1200 °C due to a low density. It increased to 20.7 in NN pellets sintered at 1300 °C. Lee et al. obtained NN ceramics with dielectric constant of 22.6 after sintering at 1150 °C using traditional oxide route.[6] Pullar et al. reported NN ceramics with dielectric constant of 21 after calcining at 1000 °C and sintering at 1200 °C via traditional oxide route.[19] As the mixed raw materials were not calcined before sintering, the grains were still small after sintering at temperatures <1250 °C as shown in Fig. 4(A) and Fig. 7. NN prepared via reaction-sintering process needs sintering temperatures 100–150 °C higher than the other reported values by Lee et al.[6] and Pullar et al.[19] Dielectric constant increased to values around 45 in NT3 and around 50 in NT4. The 30 mol% $\mathrm{TiO_2}$ addition in NN resulted in a structural change from columbite to rutile structure. This made the dielectric constant increased dramatically in NT3. Kim et al. reported dielectric constant increased slightly in $(1-x)\mathrm{ZnNb_2O_6}$–$x\mathrm{TiO_2}$ in the

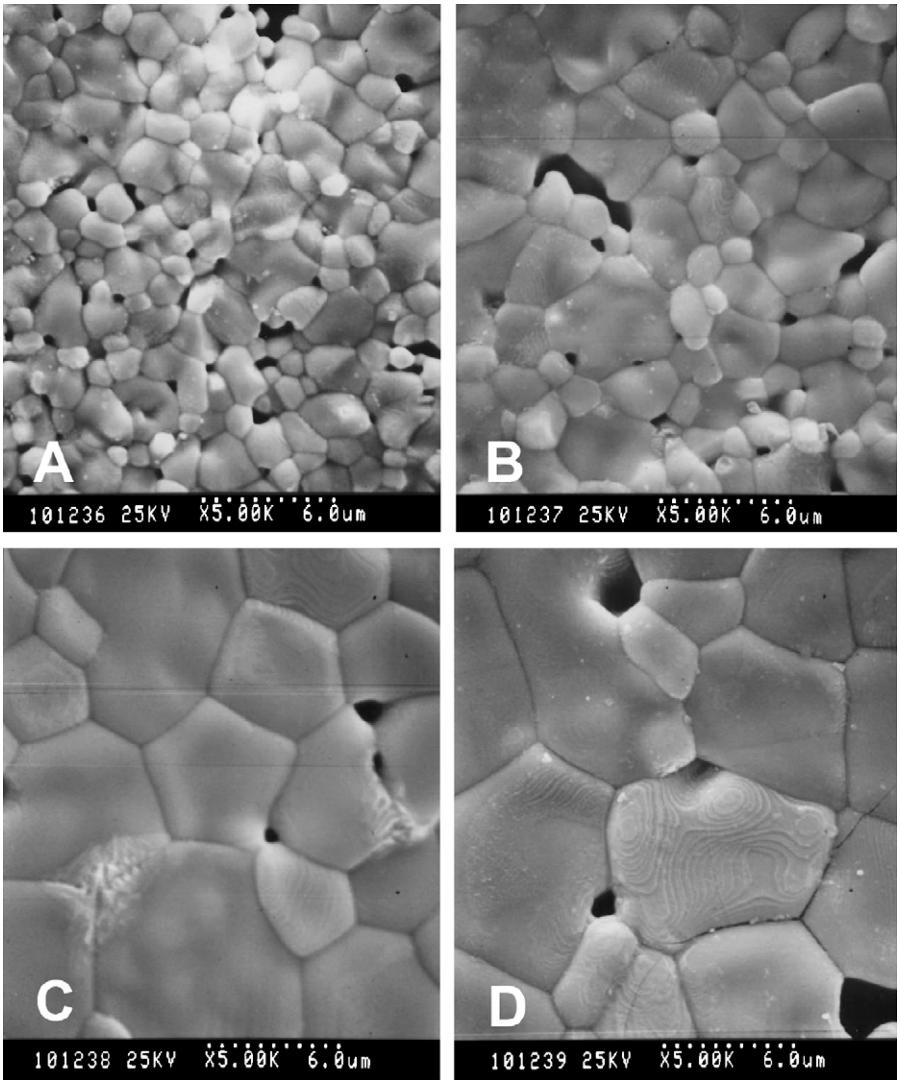

Fig. 6. SEM photographs of as-fired NT4 ceramics sintered at (A) 1200 °C, (B) 1250 °C, (C) 1300 °C, and (D) 1350 °C for 2 h.

columbite–ixiolite region ($0 < x \leq 0.54$) and increased dramatically with increasing TiO_2 content in the ixiolite and rutile regions.[10] They thought this is a result of no structural change associated with the columbite–ixiolite region. Columbite and ixiolite are isostructural, belonging to the same space group, *Pbcn*.[20,21]

$Q \times f$ of sintered NN, NT3, and NT4 pellets are shown in Fig. 9. $Q \times f$ (at 9 GHz) is 5600 GHz in NN sintered at 1200 °C

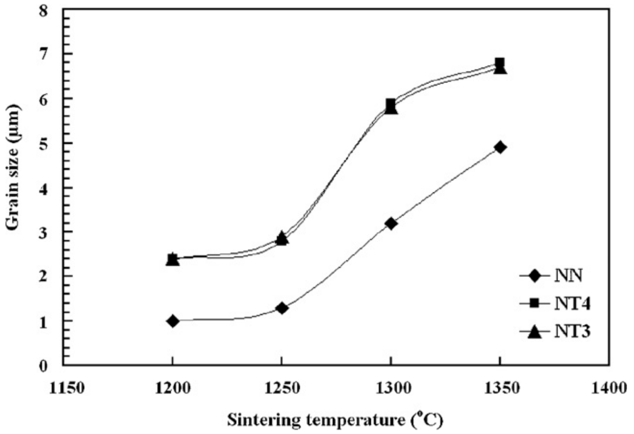

Fig. 7. Grain sizes of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h.

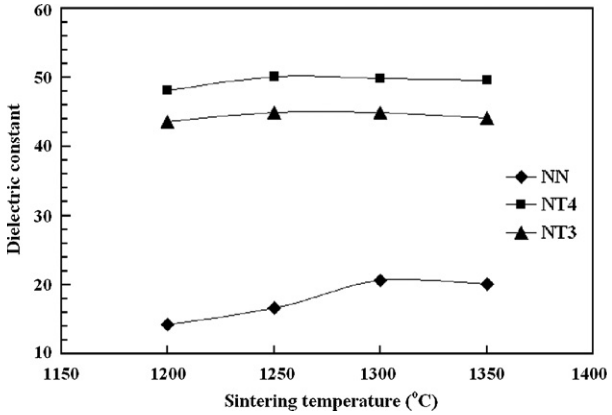

Fig. 8. Dielectric constant of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h.

Table 1
Microwave properties of NN ceramics prepared by various methods

	Proposed by		
	Lee et al.[6]	Pullar et al.[19]	This work
Processing	Mixed oxide route	Mixed oxide route	Reaction-sintering process
Calcination temperature/time	900–1050 °C/2 h	1000 °C	No calcining
Sintering temperature/time	1150 °C/2 h	1200 °C	1300 °C/2 h
ε_r	22.6	21	20.7
$Q \times f$ (GHz)	40,100	19,300	19,800
τ_f (ppm/°C)	−38	−71.3	−31.9

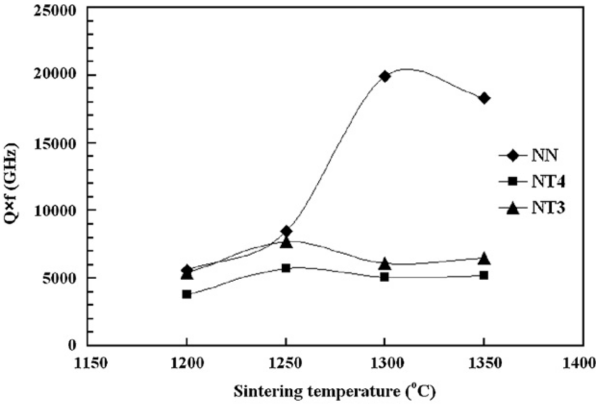

Fig. 9. $Q \times f$ values of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h.

and increases to 19,800 GHz at 1300 °C. Lee et al. reported $Q \times f$ of 40,100 GHz in NN sintered at 1150 °C.[6] Pullar et al. obtained NN with $Q \times f$ of 19,300 GHz after calcining at 1000 °C and sintering at 1200 °C via traditional oxide route.[19] $Q \times f$ (at 6 GHz) of 5400–7700 GHz in NT3 and 3800–5700 GHz in NT4 are obtained. Kim et al. reported $Q \times f$ of $(1-x)ZnNb_2O_6$–$xTiO_2$ decreased from 83,700 GHz at $x = 0$–30,000 GHz at $x = 0.54$ in the ixiolite and rutile regions.[10] τ_f of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h are shown in Fig. 10. In NN, τ_f varies linearly from −29.5 ppm/°C at 1200 °C sintering to −33.2 ppm/°C at 1350 °C sintering. Lee et al. obtained $\tau_f = -38$ ppm/°C in NN ceramics sintered at 1150 °C.[6] Pullar et al. obtained $\tau_f = -71.3$ ppm/°C in NN ceramics calcined at 1000 °C and sintered at 1200 °C via traditional oxide route.[19] The microwave dielectric properties of NN prepared using various methods are listed in Table 1 for comparison. Reaction-sintering process has proven a simple and effective method to obtain NN with good dielectric properties especially for more temperature stable NN ceramics. τ_f of ~73 ppm/°C in NT3 and ~99 ppm/°C in NT4 are obtained as shown in Fig. 10. It implies that τ_f of $Ni_{0.5}Ti_{0.5}NbO_4$ is positive and the magnitude is much greater than NN ceramics. Kim et al. reported τ_f remained constant in $(1-x)ZnNb_2O_6$–$xTiO_2$ in the columbite–ixiolite region ($0 < x \leq 0.54$) and increased dramatically with increasing TiO_2 content in the ixiolite and rutile regions. τ_f value of ~0 ppm/°C exists in the ixiolite and rutile region, at x close to 0.58.[10]

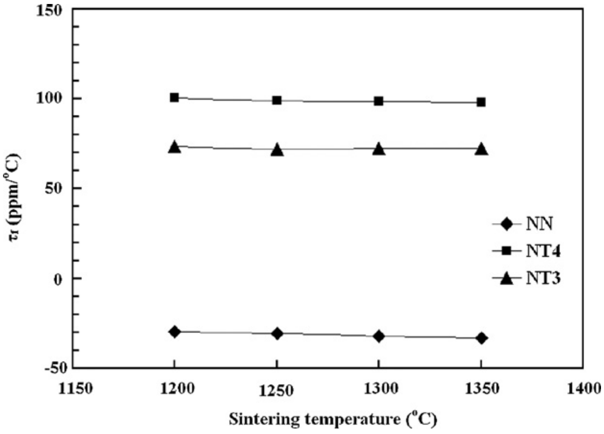

Fig. 10. τ_f of NN, NT3, and NT4 ceramics sintered at 1200–1350 °C for 2 h.

4. Conclusions

Pure columbite $NiNb_2O_6$ phase could be obtained using a reaction-sintering process with the calcinations bypassed. Phases with the same structure of $Ni_{0.5}Ti_{0.5}NbO_4$ formed in the sintered $(1-x)NiNb_2O_6$–$xTiO_2$ ceramics at $x = 0.3$ and 0.4. Maximum density 5.62 g/cm^3 (99.8% of theoretical value) for NN is found at 1300 °C/2 h sintering. Maximum density for pellets with $x = 0.3$ and 0.4 is obtained at 1350 °C/2 h sintering and reaches 4.98 g/cm^3 (95% of theoretical value) and 4.97 g/cm^3 (94.8% of theoretical value), respectively. Grain growth in pellets with $x = 0.3$ and 0.4 is easier than in the $NiNb_2O_6$ pellets. Microwave dielectric properties $\varepsilon_r = 20.7$, $Q \times f = 19{,}800$ GHz and $\tau_f = -31.9$ ppm/°C were obtained for $NiNb_2O_6$ pellets sintered at 1300 °C/2 h. ε_r around 45, $Q \times f = 5400$–7700 GHz (at 6 GHz) and $\tau_f \sim 73$ ppm/°C were obtained in pellets with 30 mol% TiO_2 addition. ε_r around 50, $Q \times f = 3800$–5700 GHz (at 6 GHz) and $\tau_f \sim 99$ ppm/°C were obtained in pellets with 40 mol% TiO_2 addition.

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