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Ceramics International 36 (2010) 1887–1892

CERAMICS INTERNATIONAL

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$Ni_4Nb_2O_9$ ceramics prepared by the reaction-sintering process

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Received 8 October 2009; received in revised form 10 February 2010; accepted 19 March 2010
Available online 28 April 2010

Abstract

Fabrication of $Ni_4Nb_2O_9$ ceramics via a reaction-sintering process was investigated. A mixture of raw materials was sintered into ceramics by bypassing calcination and subsequent pulverization stages. $Ni_4Nb_2O_9$ phase appeared at 1300 °C and increased with increasing soak time. $Ni_4Nb_2O_9$ content was found >96% in 1350 °C/2 h sintering pellets. A density of 5.71 g/cm^3 was obtained for pellets sintered at 1350 °C for 2 h. This reaches 96.5% of the theoretical density. As the sintering temperature increased to 1350 °C, an abnormal grain growth occurred and grains >100 μm could be found. ε_r of 15.4–16.9 are found in pellets sintered at 1200–1300 °C. $Q \times f$ increased from 9380 GHz in pellets sintered at 1200 °C to 14,650 GHz in pellets sintered at 1250 °C.

Keywords: $Ni_4Nb_2O_9$; Reaction-sintering process

1. Introduction

Dielectric ceramic resonators used at microwave frequencies have been widely investigated due to the fast growth of mobile communication and satellite systems. Microwave dielectric materials are required to have a high relative permittivity (ε_r), high quality factor (Q) and low temperature coefficient of resonant frequency (τ_f). Corundum-type $A_4Nb_2O_9$ (A = Mg, Co, Ni, Mn and Fe) ceramics have been studied for microwave dielectric and magnetic applications. $Mg_4Nb_2O_9$ has attracted interest due to its low dielectric loss and high dielectric constant [1–7]. Ogawa et al. found $Mg_4Nb_2O_9$ with dielectric properties: $\varepsilon_r = 11$, $Q \times f = 210{,}000$ GHz and $\tau_f = -70$ ppm/°C [5]. With the addition of perovskite $CaTiO_3$ showing $\varepsilon_r \sim 170$, $Q \times f \sim 3600$ GHz (at 7 GHz) and $\tau_f \sim 800$ ppm/°C [8], Huang et al. [9] obtained $0.5Mg_4Nb_2O_9$–$0.5CaTiO_3$ ceramics with $\varepsilon_r \sim 24.8$, $Q \times f \sim 82{,}000$ GHz (at 9.1 GHz) and $\tau_f \sim -0.3$ ppm/°C. They also reported $0.6Mg_4Nb_2O_9$–$0.4SrTiO_3$ ceramics with $\varepsilon_r \sim 21$, $Q \times f \sim 112{,}000$ GHz (at 9.7 GHz) and $\tau_f \sim 1.6$ ppm/°C [10] as perovskite $SrTiO_3$ ($\varepsilon_r \sim 205$, $Q \times f \sim 4200$ GHz and $\tau_f \sim 1700$ ppm/°C) [11] was added into $Mg_4Nb_2O_9$. Ogawa et al. obtained $Co_4Nb_2O_9$ with dielectric properties: $\varepsilon_r = 16$, $Q \times f = 5000$ GHz and $\tau_f = -10$ ppm/°C [5]. Yoshida et al. found that only solid solutions $Mg_{4-x}Ni_xNb_2O_9$ (x = 0–2) based on the $Mg_4Nb_2O_9$ structure type could be formed in the $Mg_4Nb_2O_9$–$Ni_4Nb_2O_9$ system. $Q \times f$ values decrease from 192,268 to 28,440 GHz with increasing nickel content [3]. Tarakina et al. [12] investigated crystal structure and magnetic properties of complex oxides $Mg_{4-x}Ni_xNb_2O_9$ ($0 \le x \le 4$). They found two ranges of solid solution in the system $Mg_4Nb_2O_9$–$Ni_4Nb_2O_9$. Solid solutions $Mg_{4-x}Ni_xNb_2O_9$ with a structure based on the corundum-related phase $Mg_4Nb_2O_9$ are formed at $0 \le x \le 2.75$ and a solid solution $Mg_{4-x}Ni_xNb_2O_9$ with a structure based on the II-$Ni_4Nb_2O_9$ structure is formed at $2.75 \le x \le 4$. Khamman et al. [13] prepared $Ni_4Nb_2O_9$ powders using a rapid vibro-milling technique and found minor phases of unreacted NiO and Nb_2O_5 precursors and $NiNb_2O_6$ phase tend to form together with the $Ni_4Nb_2O_9$ phase, depending on calcination conditions. Single-phase of corundum $Ni_4Nb_2O_9$ powders with particle size ranging from ~1 to 2 μm has been obtained by using a calcination temperature of 1250 °C for 2 h or 1300 °C for 0.5 h, with heating/cooling rates of 20 °C/min.

We had used a simple reaction-sintering process for $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics few years ago. A mixture of raw materials was sintered into PMN ceramics by bypassing calcination and subsequent pulverization stages. These have been the first successful synthesis of perovskite relaxor ferroelectric ceramics without the calcinations step in the

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doi:10.1016/j.ceramint.2010.03.020

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 [14]. This reaction-sintering process had also been used to produce other complex perovskite relaxor ceramics. In recent studies, we also prepared $BaTi_4O_9$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $NiNb_2O_6$, and $Mg_4Nb_2O_9$ ceramics using this process [15–18]. Microwave dielectric properties $\varepsilon_r = 20.7$, $Q \times f = 19{,}800$ GHz, and $\tau_f = -31.9$ ppm/°C were obtained for $NiNb_2O_6$ ceramics sintered at 1300 °C for 2 h [17]. While in $Mg_4Nb_2O_9$ prepared via the reaction-sintering process, minor $MgNb_2O_6$ phase were detected in $Mg_4Nb_2O_9$ sintered at 1100 and 1150 °C. $MgNb_2O_6$ phase disappeared at higher sintering temperatures and $Mg_{0.652}Nb_{0.598}O_{2.25}$ phase was detected in $Mg_4Nb_2O_9$ sintered at 1200 and 1250 °C. Maximum density 4.26 g/cm^3 (97.2% of the theoretical density) was obtained for $Mg_4Nb_2O_9$ pellets sintered at 1300 °C for 6 h. Grain size of 5–8 μm formed in $Mg_4Nb_2O_9$ pellets sintered at 1150 °C for 2 h. As the sintering temperature increased, an abnormal grain growth occurred and grains >100 μm could be found [18].

Although the corundum-type $A_4Nb_2O_9$ ceramics have been studied by some researchers, however, works of these ceramics via the reaction-sintering process are not readily available. Besides, to our knowledge, no references have been reported about microwave dielectric properties of $Ni_4Nb_2O_9$ ceramics. Therefore, we try to obtain $Ni_4Nb_2O_9$ ceramics by reaction-sintering process in this study. Phase formation, microstructures and properties were investigated.

2. Experimental procedures

All the samples in this study were prepared from reagent-grade oxides: NiO (99.8%, SHOWA, Japan) and Nb_2O_5 (99.8%, High Purity Chemicals, Japan). $Ni_4Nb_2O_9$ (NN) ceramics were weighted with the ratio $NiO/Nb_2O_5 = 4/1$ and milled in de-ionized water with zirconia balls for 12 h. After the slurry was dried and pulverized with 10 wt% poly(vinyl alcohol) (PVA) (SHOWA, Japan), the as-obtained powder was pressed into pellets with a diameter of 12 mm and thickness of 1–2 mm (6–7 mm thick for microwave properties measurement). The pellets were then heated at a rate of 10 °C/min and sintered in a covered alumina crucible at temperatures ranging from 1170 to 1350 °C for 2–6 h in air.

The sintered pellets were analyzed by X-ray diffraction (XRD) to identify the reflections of various phases. Microstructures were analyzed by scanning electron microscopy (SEM). The density of the sintered pellets was measured using the Archimedes method. The dielectric constant (ε_r) at microwave frequencies was calculated on the basis of the size of the samples and the frequency of the $TE_{0\,1\,1}$ mode using the Hakki–Coleman dielectric resonator method [19]. An Agilent 8720ES network analyzer was used to measure the frequencies.

3. Results and discussion

The XRD profiles of the NN ceramics sintered at 1170–1350 °C and the starting materials NiO and Nb_2O_5 are illustrated in Fig. 1. The reflections of $NiNb_2O_6$, matching with those in ICDD PDF #00-032-0694, were identified as the major phase in pellets sintered at lower temperatures. Some remained NiO could be found in these pellets. $Ni_4Nb_2O_9$ phase appeared at 1300 °C sintering pellets and increased obviously after sintering at 1350 °C. Therefore, the formation of $NiNb_2O_6$ phase is easier than the $Ni_4Nb_2O_9$ phase in the mixture of NiO and Nb_2O_5 during the heating up period. Quantitative ratios among $NiNb_2O_6$, $Ni_4Nb_2O_9$, and NiO phases in pellets sintered at various temperatures are listed in Table 1. $NiNb_2O_6$ content reached 61–64% in 1170–1250 °C/2 h sintering pellets. It decreased to ~56% at 1300 °C/2 h sintering and 48% at 1300 °C/4–6 h sintering. $Ni_4Nb_2O_9$ content was found >96%

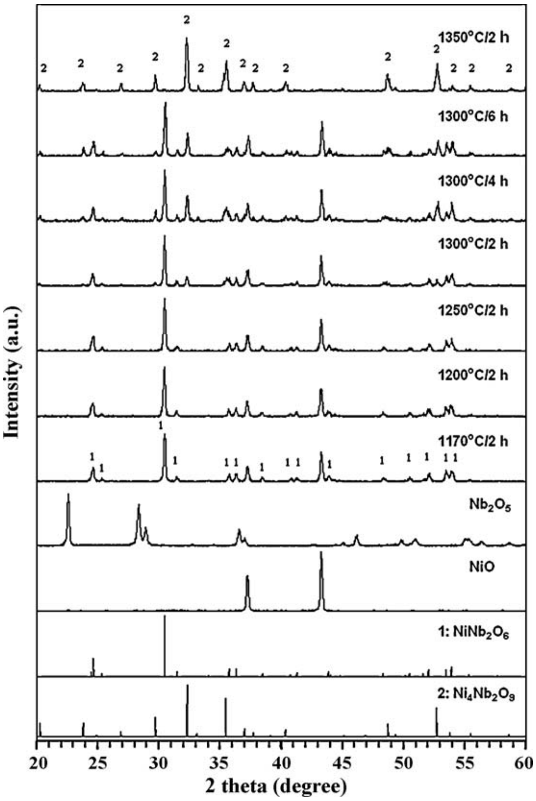

Fig. 1. XRD patterns of NN ceramics sintered at 1170–1350 °C and the starting materials NiO and Nb_2O_5. 1: $NiNb_2O_6$ (ICDD PDF #00-032-0694) and 2: $Ni_4Nb_2O_9$ (ICDD PDF #01-077-2409).

Table 1
Quantitative ratios among $NiNb_2O_6$, $Ni_4Nb_2O_9$, and NiO phases in pellets sintered at various temperatures.

Sintering temperature	$NiNb_2O_6$	$Ni_4Nb_2O_9$	NiO
1170 °C/2 h	61.65%	0.24%	38.11%
1200 °C/2 h	64.12%	0.57%	35.31%
1250 °C/2 h	62.43%	0.27%	37.30%
1300 °C/2 h	55.98%	10.43%	33.59%
1300 °C/4 h	48.06%	22.69%	29.25%
1300 °C/6 h	48.00%	20.57%	31.43%
1350 °C/2 h	1.54%	96.04%	2.42%

% of $NiNb_2O_6 = I_1/(I_1 + I_2 + I_3) \times 100\%$; % of $Ni_4Nb_2O_9 = I_2/(I_1 + I_2 + I_3) \times 100\%$; % of $NiO = I_3/(I_1 + I_2 + I_3) \times 100\%$; I_1 = intensity of the major peak of $NiNb_2O_6$ at 2θ around 30.44°; I_2 = intensity of the major peak of $Ni_4Nb_2O_9$ at 2θ around 32.3°; I_3 = intensity of the major peak of NiO at 2θ around 43.3°.

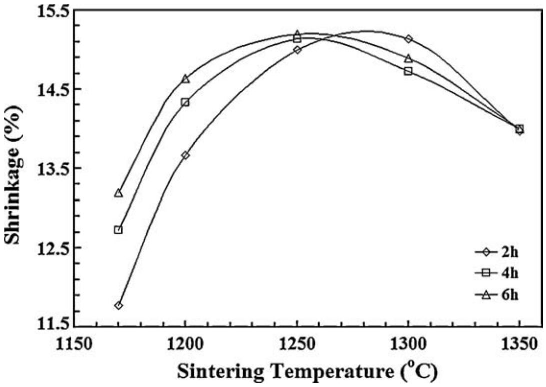

Fig. 2. Shrinkage percentages of NN ceramics sintered at various temperatures for 2–6 h.

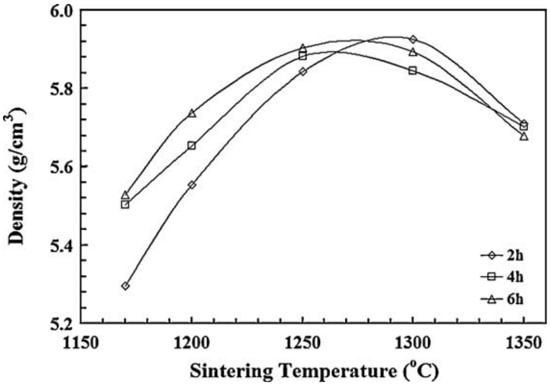

Fig. 3. Density of NN ceramics sintered at various temperatures for 2–6 h.

in 1350 °C/2 h sintering pellets. Ehrenberg et al. [20] obtained $Ni_4Nb_2O_9$ with trifling impurities NiO and $NiNb_2O_6$ after heating the mixture of NiO and Nb_2O_5 in flowing oxygen at 1450 °C for 48 h. In the calcined $Ni_4Nb_2O_9$ powder, Khamman et al. found that $NiNb_2O_6$ phase appeared at 600 °C and became the predominant phase in the powder calcined above 800 °C, mixing with NiO and Nb_2O_5 phases. A single-phase $Ni_4Nb_2O_9$ powder formed after calcining at 1250 °C and 1300 °C [13]. From the discussion above, the reaction-sintering process is proven a simple and effective process to obtain NN ceramics. In our study of $Mg_4Nb_2O_9$ ceramics prepared by a reaction-sintering process, $Mg_4Nb_2O_9$ were identified as the major phase and some weak peaks corresponding to $MgNb_2O_6$ phase were detected in pellets sintered at 1100 and 1150 °C. These peaks disappeared in pellets sintered at higher temperatures and some weak peaks corresponding to $Mg_{0.652}Nb_{0.598}O_{2.25}$ were detected in pellets sintered at 1200 and 1250 °C [18]. This implies that formation of $Ni_4Nb_2O_9$ phase is more difficult than $Mg_4Nb_2O_9$ phase when the reaction-sintering process was used.

Fig. 2 illustrates the linear shrinkage of the NN ceramics sintered at various temperatures. Shrinkage values 11.8–15.2% are found at 1170–1350 °C. In our study of $NiNb_2O_6$ ceramics prepared by a reaction-sintering process, a shrinkage value 16.7% was found in pellets sintered at 1200 °C/2 h [17].

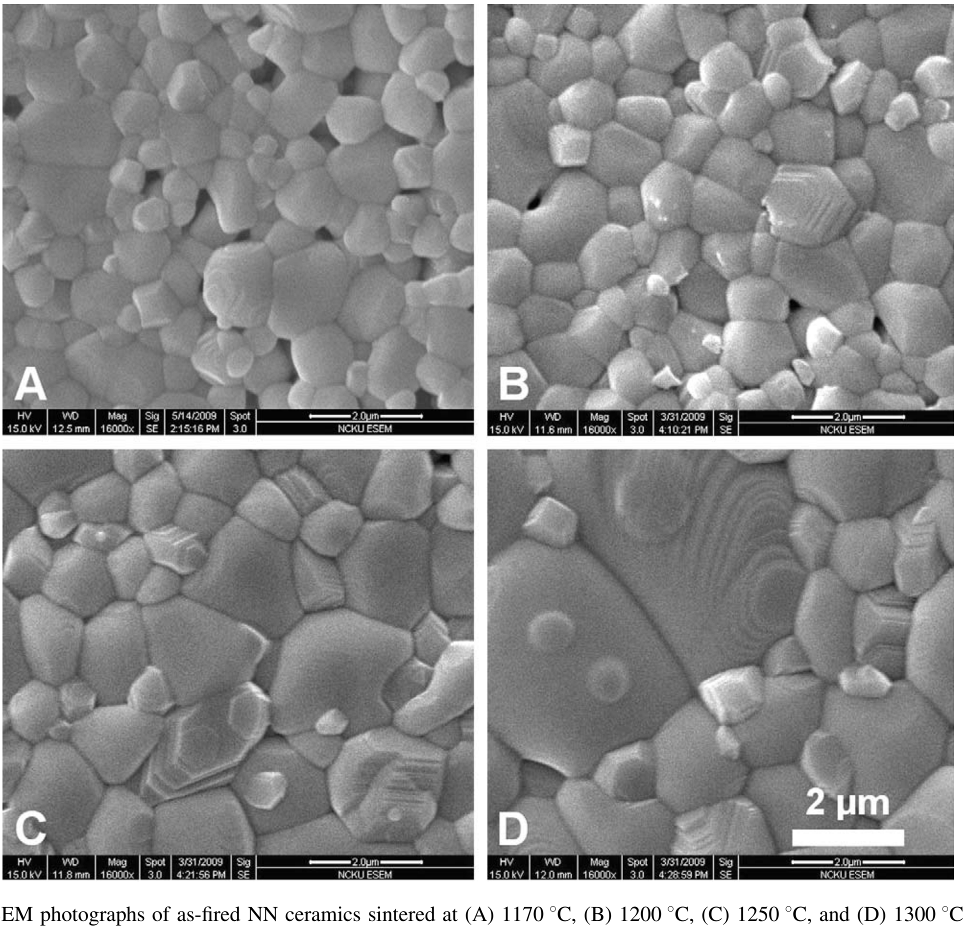

Fig. 4. SEM photographs of as-fired NN ceramics sintered at (A) 1170 °C, (B) 1200 °C, (C) 1250 °C, and (D) 1300 °C for 2 h.

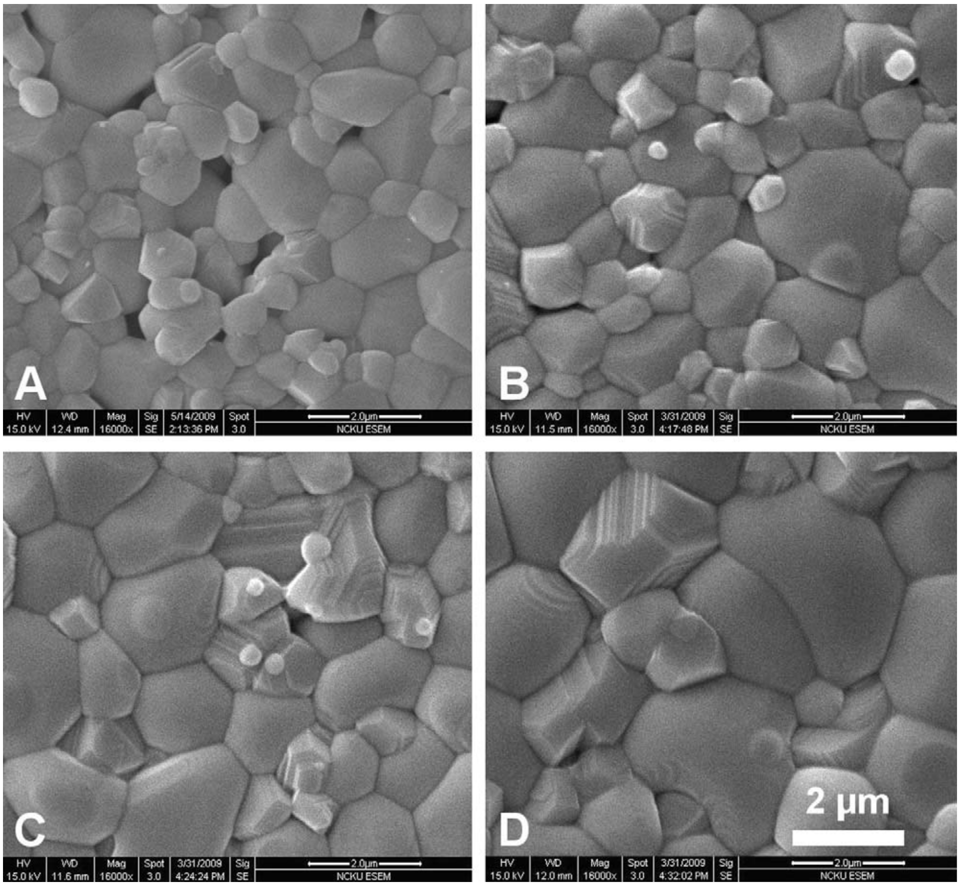

Fig. 5. SEM photographs of as-fired NN ceramics sintered at (A) 1170 °C, (B) 1200 °C, (C) 1250 °C, and (D) 1300 °C for 4 h.

A similar trend was observed for the density values as shown in Fig. 3. A density of 5.71 g/cm^3 was obtained for pellets sintered at 1350 °C for 2 h. This reaches 96.5% of the theoretical density 5.915 g/cm^3 of NN ceramic. Yoshida et al. found 90.3–93.7% of the theoretical density in $Mg_{4-x}Ni_xNb_2O_9$ ($x = 0.5$–2) after calcining at 1000 °C for 20 h and sintering at 1200–1500 °C for 10 h [3]. Therefore, the reaction-sintering process is proven a simple and effective process to obtain dense NN ceramics. In $NiNb_2O_6$ ceramics prepared by a reaction-sintering process, maximum density 5.62 g/cm^3 (99.8% of theoretical value) was found at 1300 °C/2 h sintering [17]. In our study of $Mg_4Nb_2O_9$ ceramics prepared by a reaction-sintering process, pellets with 97.2% of the theoretical density were obtained after sintering at 1300 °C for 6 h [18]. This implies that densification in $Ni_4Nb_2O_9$ ceramic is more difficult than $NiNb_2O_6$ and $Mg_4Nb_2O_9$ when the reaction-sintering process was used.

SEM photographs of as-fired NN ceramics sintered at 1170–1300 °C for 2 h are presented in Fig. 4. Porous pellet with grains <2 μm is observed for 1170 °C sintering. Pores decreased and grain size increased as sintering temperature increased. Grains >6 μm could be found in pellets sintered at 1300 °C. This shows a good agreement with the results of density in Fig. 3. In $NiNb_2O_6$ via reaction-sintering process, grains less than 2 μm were observed in pellets sintered at 1250 °C/2 h and still <6 μm in pellets sintered at 1350 °C/2 h [17] indicating the grain growth in NN ceramics is easier than $NiNb_2O_6$ even though the formation and densification are more difficult. While in $Mg_4Nb_2O_9$ via reaction-sintering

Table 2
Grain size of NN pellet sintered at various temperatures and soak times.

Sintering temperature	2 h (μm)	4 h (μm)
1170 °C	0.97	1.36
1200 °C	1.33	1.64
1250 °C	1.91	2.03
1300 °C	2.64	2.84

Table 3
ε_r and $Q \times f$ of NN ceramics sintered at various temperatures for 2 h.

	Sintering temperature			
	1200 °C	1250 °C	1300 °C	1350 °C
ε_r	15.4	16.9	15.9	13.2
$Q \times f$	9380 GHz (at 9.7 GHz)	14,650 GHz (at 9.5 GHz)	11,650 GHz (at 9.8 GHz)	14,610 GHz (at 10.5 GHz)

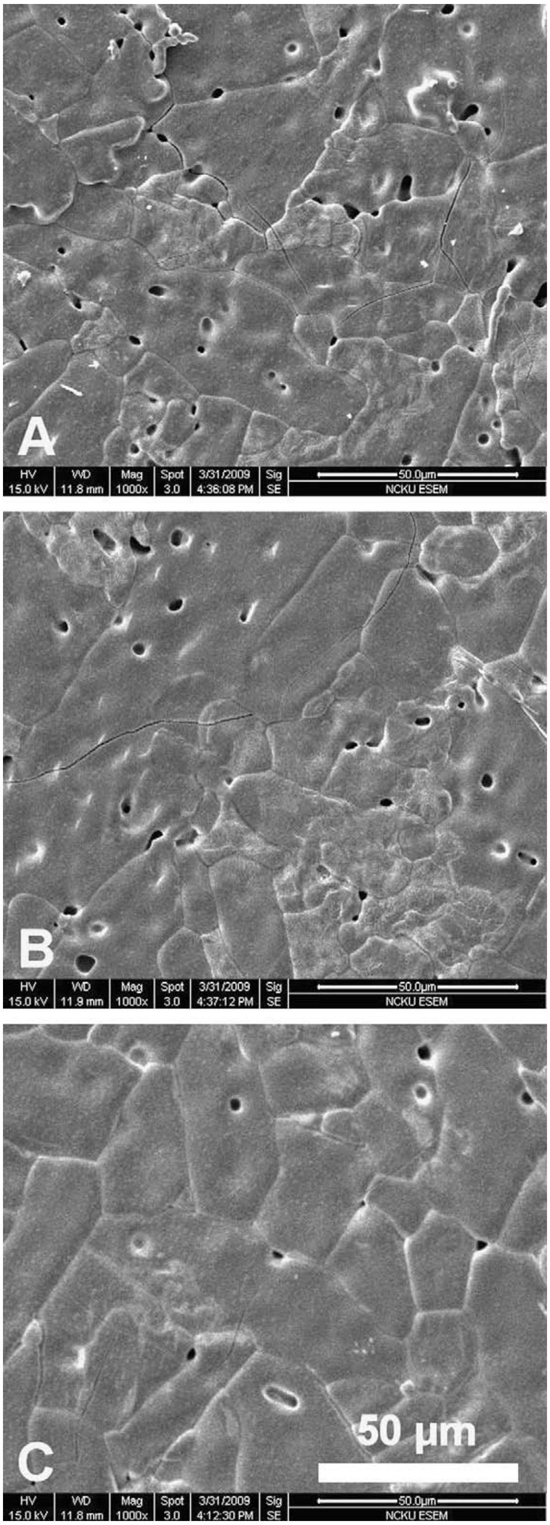

Fig. 6. SEM photographs of as-fired NN ceramics sintered at 1350 °C for (A) 2 h, (B) 4 h, and (C) 6 h.

process, 5–8 μm grains formed in pellets sintered at 1150 °C/2 h [18]. Grain size increased in NN pellets sintered for 4 h as shown in Fig. 5. The average grain sizes for NN ceramics in Figs. 4 and 5 are listed in Table 2. As the sintering temperature increased to 1350 °C, an abnormal grain growth occurred and grains >100 μm could be found in Fig. 6. Similar abnormal grain growth was also observed in $Mg_4Nb_2O_9$ via reaction-sintering process, grains >100 μm were observed in pellets sintered at 1200–1300 °C [18]. Kan and Ogawa [7] also found grains >40 μm in Mg_4NbSbO_9 ceramics after calcining at 1100 °C for 10 h then sintering at 1500 and 1600 °C for 10 h.

ε_r and $Q \times f$ of NN ceramics sintered at various temperatures for 2 h are listed in Table 3. ε_r of 15.4–16.9 are found in pellets sintered at 1200–1300 °C and decreases to 13.2 in pellets sintered at 1350 °C. In $NiNb_2O_6$ via reaction-sintering process, $\varepsilon_r = 20.7$ was obtained after sintering at 1300 °C/2 h [17]. Yoshida et al. found ε_r decreased from 12.8 to 11.1 with increasing nickel content in $Mg_{4-x}Ni_xNb_2O_9$ ($x = 0.5$–2) after calcining at 1000 °C for 20 h and sintering at 1200–1500 °C for 10 h [3]. Therefore, the decrease of ε_r in pellets sintered at 1350 °C is due to the increased $Ni_4Nb_2O_9$ content. $Q \times f$ increased from 9380 GHz in pellets sintered at 1200 °C to 14,650 GHz in pellets sintered at 1250 °C mainly resulted from the increased density. $Q \times f$ decreased to 11,650 GHz in pellets sintered at 1300 °C due to the formation of $Ni_4Nb_2O_9$ phase (shown in Fig. 1 and Table 1) and the inhomogeneous microstructure (shown in Fig. 4). Yoshida et al. found $Q \times f$ decreased from 84,270 to 28,440 GHz with increasing nickel content in $Mg_{4-x}Ni_xNb_2O_9$ ($x = 0.5$–2) after calcining at 1000 °C for 20 h and sintering at 1200–1500 °C for 10 h [3].

4. Conclusions

The reaction-sintering process is a simple and effective method for obtaining $Ni_4Nb_2O_9$ ceramics. $Ni_4Nb_2O_9$ phase appeared at 1300 °C and increased with increasing soak time. $Ni_4Nb_2O_9$ content was found >96% in 1350 °C/2 h sintering pellets. Shrinkage values 11.8–15.2% are found at 1170–1350 °C. A density of 5.71 g/cm^3 was obtained for pellets sintered at 1350 °C for 2 h. This reaches 96.5% of the theoretical density. Densification in $Ni_4Nb_2O_9$ ceramic is more difficult than $NiNb_2O_6$ and $Mg_4Nb_2O_9$ when the reaction-sintering process was used. Porous pellet with grains <2 μm is observed for 1170 °C sintering. Grains > 6 μm could be found in pellets sintered at 1300 °C. As the sintering temperature increased to 1350 °C, an abnormal grain growth occurred and grains >100 μm could be found. ε_r of 15.4–16.9 are found in pellets sintered at 1200–1300 °C and decreases to 13.2 in pellets sintered at 1350 °C. $Q \times f$ increased from 9380 GHz in pellets sintered at 1200 °C to 14,650 GHz in pellets sintered at 1250 °C.

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