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Preparation of columbite $MgNb_2O_6$ and $ZnNb_2O_6$ ceramics by reaction-sintering

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Abstract

Columbite $MgNb_2O_6$ (MN) and $ZnNb_2O_6$ (ZN) ceramics produced by the reaction-sintering process were investigated. Secondary phases $Mg_{0.652}Nb_{0.598}O_{2.25}$ and $Mg_{0.66}Nb_{11.33}O_{29}$ were found in $MgNb_2O_6$ pellets. After 1250 °C sintering for 2 h, a density 4.85 g/cm^3 (97.1% of the theoretical value) was obtained in $MgNb_2O_6$ pellets. In $ZnNb_2O_6$ pellets, no secondary phase formed. The maximum density 5.55 g/cm^3 (98.7% of the theoretical value) occurs at 1200 and 1180 °C sintering for 2 and 4 h, respectively.

Keywords: $MgNb_2O_6$; $ZnNb_2O_6$; Reaction-sintering process

1. Introduction

Microwave dielectric ceramics have been widely investigated for the use of resonators and filters in the satellite and mobile communication systems. Complex perovskite compounds $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) exhibit excellent microwave dielectric properties [1,2]. However, temperatures are fairly high in sintering these complex perovskite ceramics. Besides, raw material Ta_2O_5 is expensive as compared with Nb_2O_5. MNb_2O_6 (where M = Mg, Zn, Ni, Ca, Cu, Mn and Co) columbite niobate compounds of low sintering temperature and low cost have received much attention [3–6]. $ZnNb_2O_6$ (ZN) ceramics were reported to exhibit excellent dielectric properties ($\varepsilon_r = 25$, $Q \times f = 83{,}700$ GHz and $\tau_f = -56.1$ ppm/°C). For the $MgNb_2O_6$ (MN) ceramics, $\varepsilon_r \sim 21.4$, $Q \times f \sim 93{,}800$ GHz and $\tau_f \sim -70$ ppm/°C were reported [4]. Therefore, columbite niobate compounds are investigated for the applications in microwave dielectric resonators.

Recently, Liou and co-workers prepared $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics by a simple and effective reaction-sintering process [7,8]. The mixture of PbO, $Mg(NO_3)_2$, $Fe(NO_3)_3$ and Nb_2O_5 was pressed and sintered directly into PMN and PFN ceramics with the calcination step

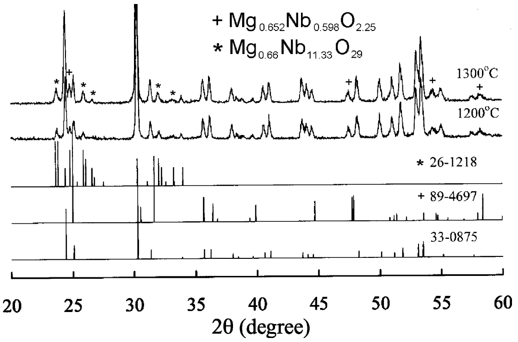

Fig. 1. XRD profiles of MN ceramics sintered at 1200 and 1300 °C for 2 h.

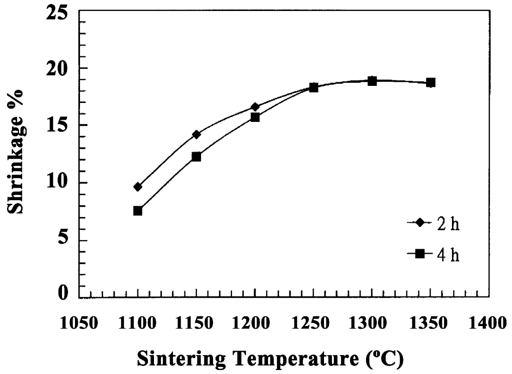

Fig. 2. Shrinkage percentage of MN ceramics sintered at various temperatures and soak time.

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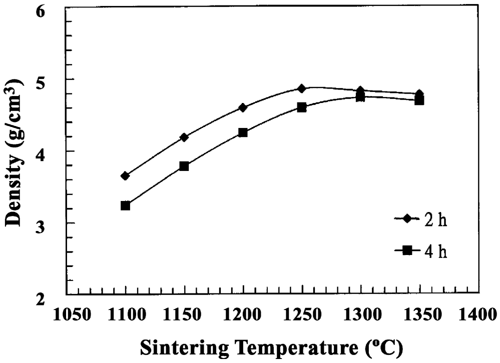

Fig. 3. Density of MN ceramics sintered at various temperatures and soak time.

Table 1
Mean grain sizes (μm) of MN ceramics sintered at various temperatures for 2 h and 4 h

Sintering temperature (°C)	Mean grain sizes (μm)	
	2 h	4 h
1150	0.4	1.1
1200	1.2	2.3
1250	2.5	3.7
1300	3.6	4.2

bypassed. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step in the conventional mixed oxide route or in the columbite/wolframite route (two calcination steps were involved). PMN ceramics with a density of 8.09 g/cm^3 and dielectric constant 19,900 (1 kHz) are obtained. Other Pb-based complex perovskite ceramics were also produced by this reaction-sintering process, successfully. In recent studies, some microwave dielectric ceramics such as $BaTi_4O_9$, $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$, $Ba_5Nb_4O_{15}$ and $Sr_5Nb_4O_{15}$ were also prepared successfully by this reaction-sintering process [9–11].

In this study, the authors try to obtain $MgNb_2O_6$ and $ZnNb_2O_6$ columbite ceramics by the reaction-sintering process.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: MgO (98%, Showa, Japan), ZnO (99%, Showa, Japan) and Nb_2O_5 (99.8%, High Purity Chemicals, Japan). Appropriate amounts of raw materials for stoichiometric

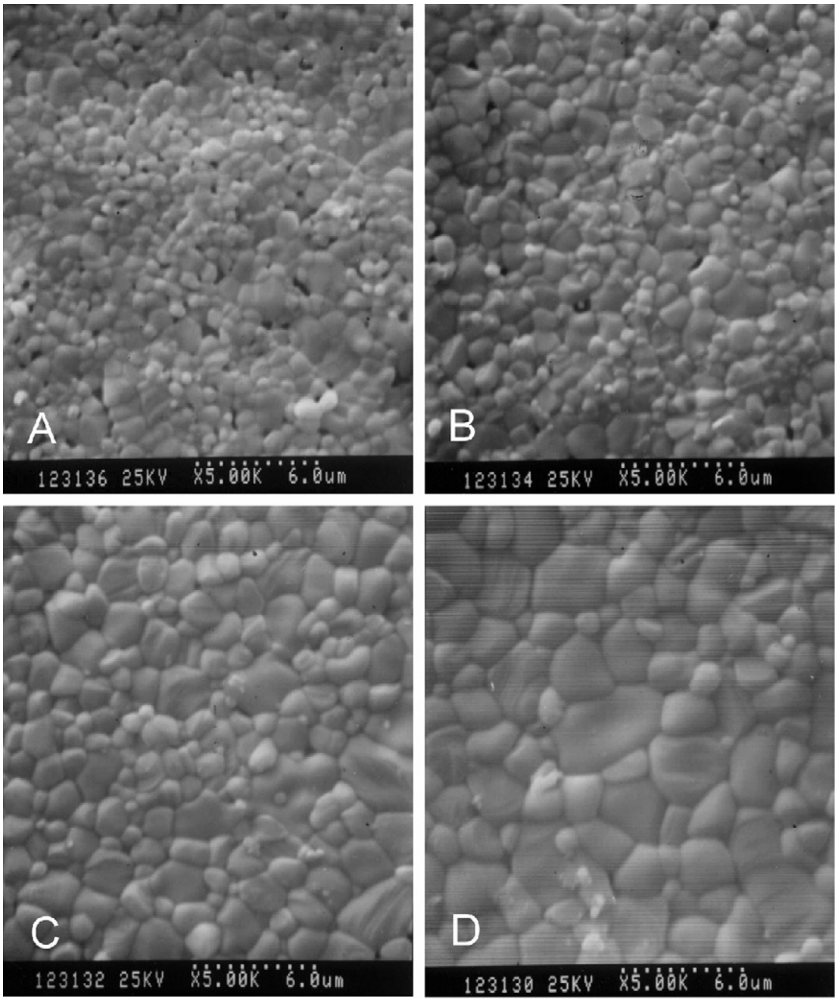

Fig. 4. SEM photographs of as-fired MN ceramics sintered at: (A) 1150 °C, (B) 1200 °C, (C) 1250 °C and (D) 1300 °C for 2 h.

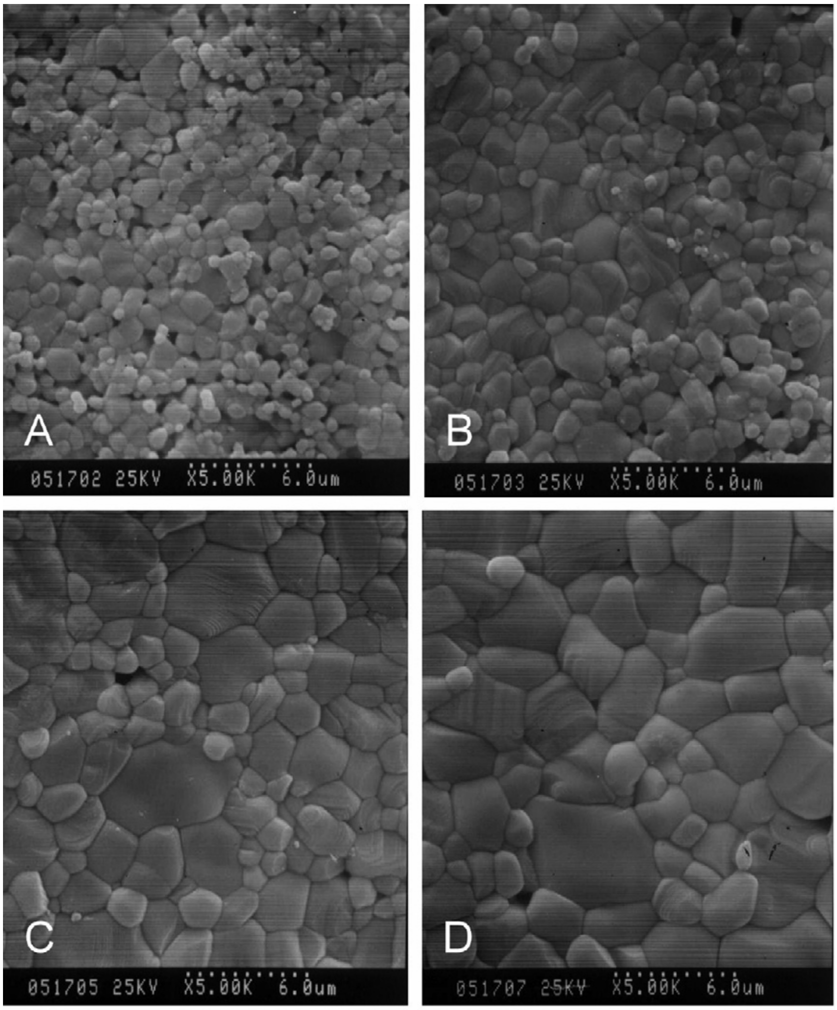

Fig. 5. SEM photographs of as-fired MN ceramics sintered at: (A) 1150 °C, (B) 1200 °C, (C) 1250 °C and (D) 1300 °C for 4 h.

$MgNb_2O_6$ and $ZnNb_2O_6$ were weighted and milled in acetone with zirconia balls for 12 h. After the slurry was dried and pulverized, the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were then heated at a rate 10 °C/min and sintered in covered alumina crucible at temperatures ranging from 1050 to 1350 °C for 2 and 4 h in air.

The sintered pellets were analyzed by X-ray diffraction (XRD) to check the formed phases. The density of sintered pellets was measured by the Archimedes method. Microstructures were analyzed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. $MgNb_2O_6$

Fig. 1 shows the XRD profiles of MN ceramics sintered at 1200 and 1300 °C for 2 h. These reflections match with those of $MgNb_2O_6$ in JCPDS file no. 33-0875. This proves the columbite phase $MgNb_2O_6$ could be obtained by the reaction-sintering process. This simple process is effective not only in preparing $BaTi_4O_9$, $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$ and Pb-based complex perovskite ceramics but also effective in preparing columbite $MgNb_2O_6$ ceramics. Some reflections of secondary phases are also found in the profiles. These are $Mg_{0.652}Nb_{0.598}O_{2.25}$ and $Mg_{0.66}Nb_{11.33}O_{29}$ phases match with JCPDS file no. 89-4697 and file no. 26-1218, respectively. In the study of Srisombat

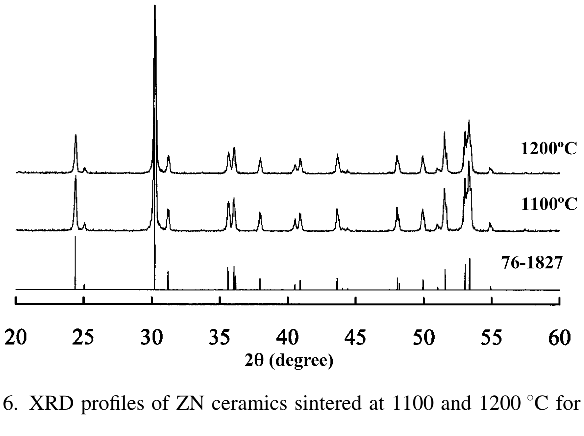

Fig. 6. XRD profiles of ZN ceramics sintered at 1100 and 1200 °C for 2 h.

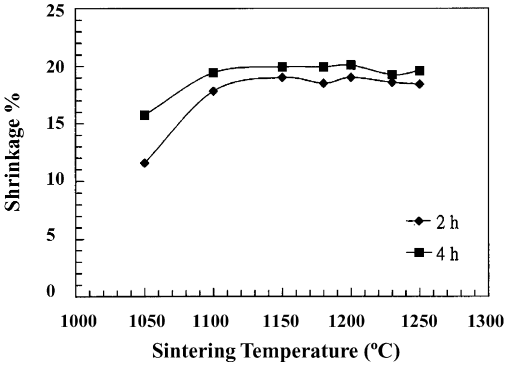

Fig. 7. Shrinkage percentage of ZN ceramics sintered at various temperatures and soak time.

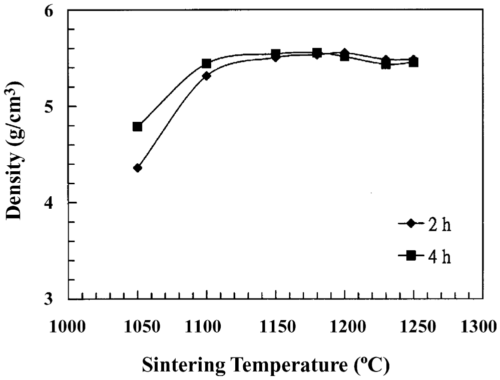

Fig. 8. Density of ZN ceramics sintered at various temperatures and soak time.

et al. [12], $Mg_{0.66}Nb_{11.33}O_{29}$ phase was formed in MN powder prepared via an oxalate synthetic route. In many previous studies, $Mg_4Nb_2O_9$ phase was the secondary phase formed in MN powder via the conventional solid-state reaction process and the citrate-gel method [13–16]. In our study of $NiNb_2O_6$ (NN) prepared by reaction-sintering process, the secondary phase $Ni_4Nb_2O_9$ was found [17]. This implies that secondary phases formed in preparing columbite phase are different in different processes. The shrinkage percentage of MN pellet increases from 1100 °C and saturates at temperatures above 1250 °C as shown in Fig. 2. It indicates a full sintering occurred at 1250 °C and is the same as NN ceramics [17].

In Fig. 3, the density of 2 h sintering MN ceramics increases with sintering temperature and reaches a maximum value 4.85 g/cm^3 (97.1% of the theoretical value) at 1250 °C then slightly decreased. Similar results are obtained in pellets

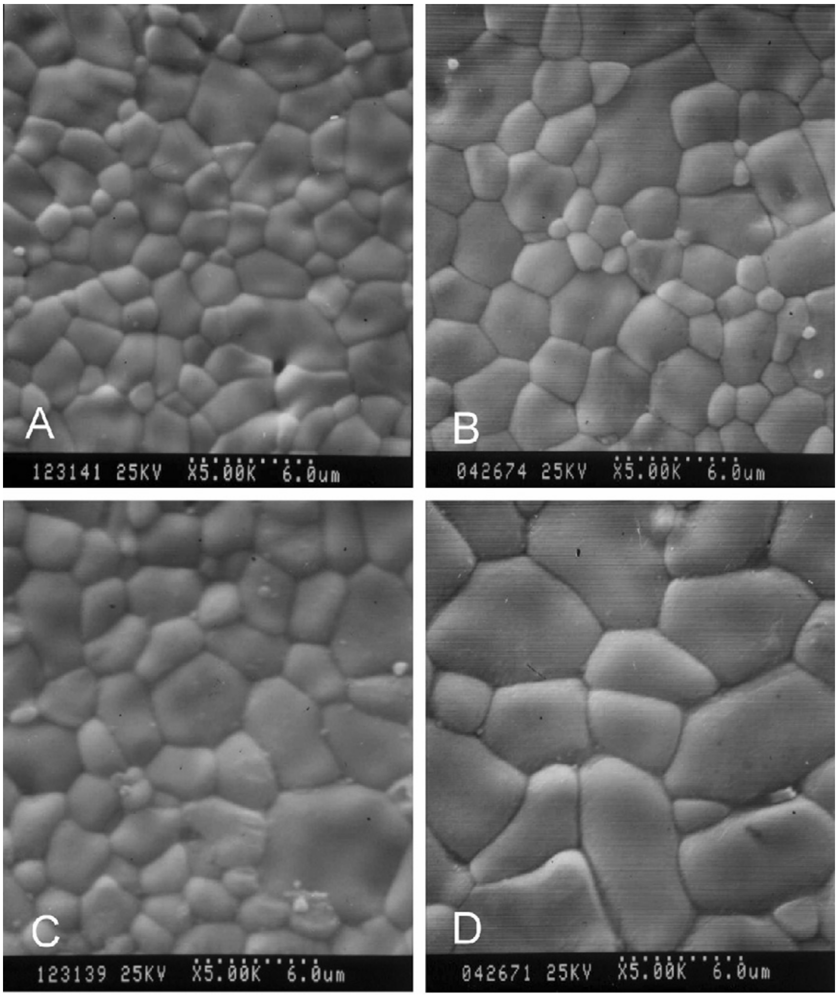

Fig. 9. SEM photographs of as-fired ZN ceramics sintered at: (A) 1150 °C, (B) 1180 °C, (C) 1200 °C and (D) 1230 °C for 2 h.

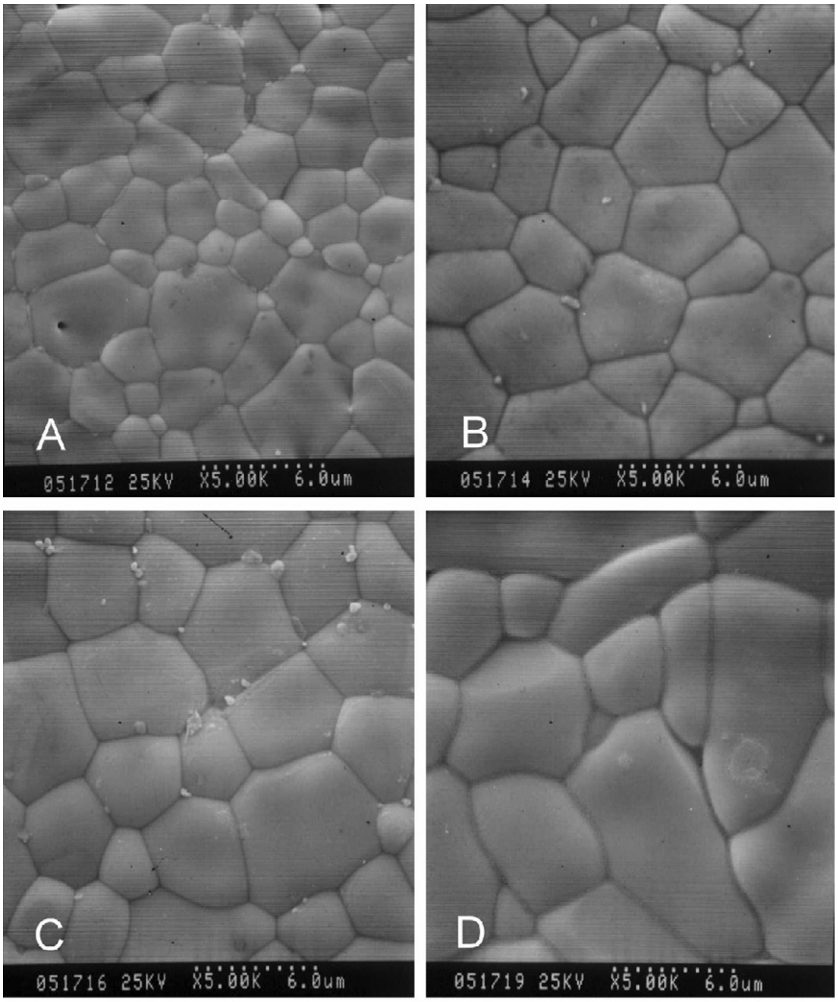

Fig. 10. SEM photographs of as-fired ZN ceramics sintered at: (A) 1100 °C, (B) 1150 °C, (C) 1180 °C and (D) 1230 °C for 4 h.

sintered for 4 h and the maximum density at 1300 °C decreased to 4.73 g/cm^3. In the study of Thirumal and Ganguli, a density close to 96% of the theoretical value was obtained in MN ceramics calcined at 1100 °C for 30 h and sintered at 1200–1250 °C for 24–36 h [18]. Hsu et al. reported a maximum density of 4.85 g/cm^3 in 1 wt% CuO added MN ceramics after calcined at 1150 °C for 2 h and sintered at 1170 °C for 3 h [6]. Therefore, reaction-sintering process is effective to produce MN ceramics with high density even without the calcination and the sintering aid. The SEM photos of MN ceramics sintered at 1150–1300 °C for 2 h are shown in Fig. 4. Grains began to grow at 1150 °C and the size increased significantly with the sintering temperature. As shown in Fig. 5, larger grains are found in pellets sintered for 4 h. Round grains are observed and are different from those rod-like grains in other study [6]. In the study of Srisombat et al. [12], rod-like calcined $Mg_{0.66}Nb_{11.33}O_{29}$ grains were formed in MN powder prepared via an oxalate synthetic route. The mean grain sizes are listed in Table 1. The 0.4–4.2 μm grains were formed in MN pellets sintered at 1150–1300 °C for 2 and 4 h. As compared with NN prepared by reaction-sintering process, grain growth in MN is easier than in NN [17].

3.2. $ZnNb_2O_6$

The XRD profiles of ZN ceramics sintered at 1100 and 1200 °C for 2 h are shown in Fig. 6. The reflections match with those of $ZnNb_2O_6$ in JCPDS file no. 76-1827 and no secondary phase is observed. It indicates that pure phased columbite $ZnNb_2O_6$ ceramics could be obtained by reaction-sintering process. The shrinkage percentage of ZN pellet increases from 1050 °C and saturates at temperatures above 1100 °C as shown in Fig. 7. Full sintering occurs at 1100 °C and is 150 °C lower than MN and NN [17]. Fig. 8 shows the variation of density with sintering temperature. It increases from 1050 °C and saturates at temperatures higher than 1100 °C. The maximum value 5.55 g/cm^3 (98.7% of the theoretical density) occurs at 1200 and 1180 °C sintering for 2 and 4 h, respectively. The degree of densification is higher than MN but lower than NN. In NN ceramics prepared by reaction-sintering process, 99.8% of the theoretical density was obtained [17]. Pullar et al. reported a relative density of 94.4% in ZN after calcined at 1000–1200 °C for 12 h and sintered at 1200 °C for 2 h [19]. Zhang et al. obtained a density of ZN close to 97% with 0.5 wt% CaF_2 addition after calcined at 1000 °C for 2 h and sintered at

1080 °C for 2 h [20]. Therefore, reaction-sintering process is effective to produce ZN ceramics with high density even without the calcination and the sintering aid.

Table 2
Mean grain sizes (μm) of ZN ceramics sintered at various temperatures for 2 h and 4 h

Sintering temperature (°C)	Mean grain sizes (μm)	
	2 h	4 h
1100	0.9	3.6
1150	3.5	4.4
1180	3.8	4.9
1200	4.1	5.5
1230	5.9	6.5
1250	6.3	6.9

Porous pellets with fine grains formed in ZN sintered at 1050 °C for 2 h and the pores decreased significantly at 1100 °C in consistent with the shrinkage percentage shown in Fig. 7. In Fig. 9, pores are not found in pellets sintered at 1150–1230 °C. Round grains formed at 1150–1200 °C and some long column shape grains are found at 1230 °C. The amount and the length in major axis direction of these long column shape grains increase at 1250 °C. In other studies, long shaped grains are mostly observed in ZN ceramics prepared by the conventional oxide route or the mechnochemical processing [21,22]. Fig. 10 shows the SEM photos of ZN pellets sintered for 4 h. Much larger grains are clearly observed and the long shaped grains are found only at 1230 °C. Therefore, the morphology in microstructure of ZN prepared by reaction-sintering process is different from ZN prepared by the conventional oxide route or the mechnochemical processing. The major difference between reaction-sintering process and other processes is that the particles in the pressed pellets before heated for sintering are not highly agglomerated clusters as those in calcined or high-energy milled powders. These highly agglomerated micro-grains begin to grow at a certain temperature during the heating up period. There are enough spaces between clusters for the long shaped grain to grow. While in reaction-sintering process, particles begin to react with each other then the nucleation occurs and the pellet is entirely agglomerated. There is no space for the long shaped grain to grow because it is clamped closely by the surrounding micro-grains. This is illustrated by the SEM photos of ZN pellets sintered at 1050 and 1100 °C shown in Fig. 11. Highly agglomerated micro-grains

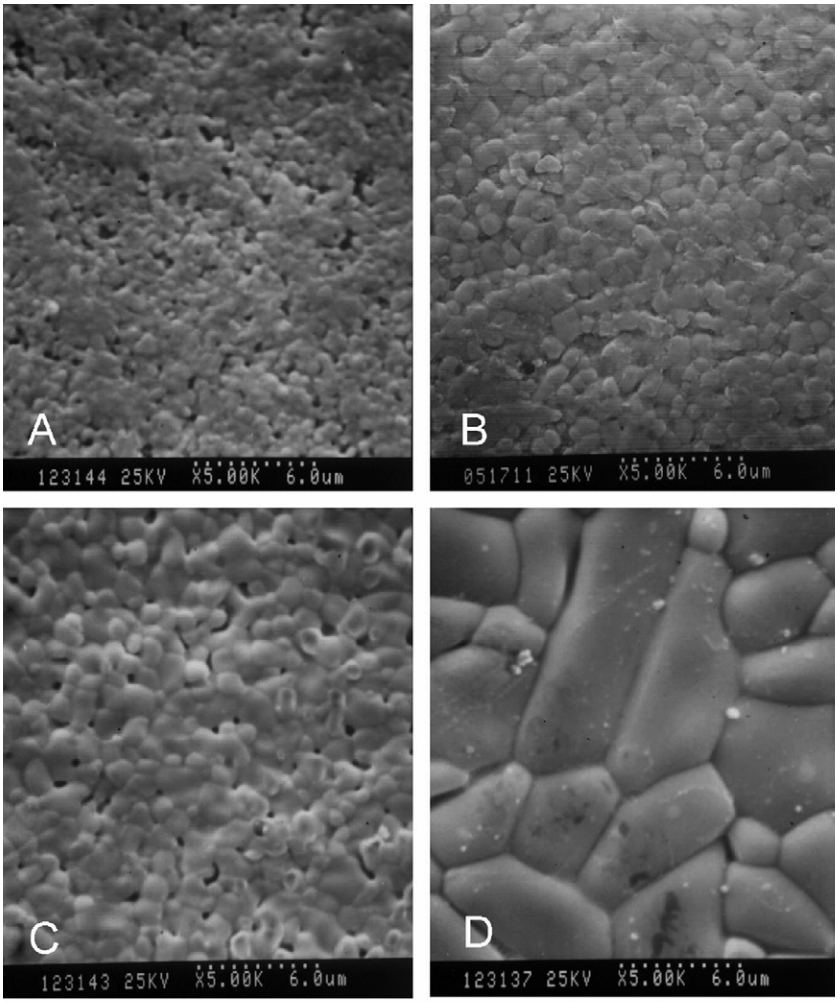

Fig. 11. SEM photographs of as-fired ZN ceramics sintered at: (A) 1050 °C/2 h, (B) 1050 °C/4 h, (C) 1100 °C/2 h and (D) 1250 °C/2 h.

formed after sintered at 1050 °C for 2 h and the grains became larger at higher temperature or longer soak time. The long shaped grain formed only when a high enough driving force at higher temperature occurred to overcome the clamping force of the surrounding grains. The mean grain sizes are listed in Table 2. The 0.9–6.9 μm grains were formed in ZN pellets sintered at 1100–1250 °C for 2 and 4 h. These are much larger than grains formed in MN and NN [17] prepared by reaction-sintering process. As compared with other processes, grains are smaller than those by conventional oxide route [23] and larger than those by the mechnochemical processing [21].

4. Conclusions

Columbite $MgNb_2O_6$ and $ZnNb_2O_6$ phases were obtained successfully by a reaction-sintering process. Secondary phases $Mg_{0.652}Nb_{0.598}O_{2.25}$ and $Mg_{0.66}Nb_{11.33}O_{29}$ are found in $MgNb_2O_6$ pellets. After 1250 °C sintering for 2 h, a density 4.85g/cm^3 (97.1% of the theoretical value) was obtained in $MgNb_2O_6$ pellets. The 0.4–4.2 μm grains were formed in $MgNb_2O_6$ pellets sintered at 1150–1300 °C for 2 and 4 h. No secondary phase formed in $ZnNb_2O_6$ pellets. The maximum density 5.55 g/cm^3 (98.7% of the theoretical value) occurs at 1200 and 1180 °C sintering for 2 and 4 h, respectively. Round grains formed at 1150–1200 °C and some long column shape grains are found at 1230 °C. The amount and the length in major axis direction of these long column shape grains increase at 1250 °C. The 0.9–6.9 μm grains were formed in $ZnNb_2O_6$ pellets sintered at 1100–1250 °C for 2 and 4 h.

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