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Synthesis of $Zn_3Nb_2O_8$ ceramics using a simple and effective process

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Abstract

Synthesis of $Zn_3Nb_2O_8$ ceramics using a simple and effective reaction-sintering process was investigated. The mixture of ZnO and Nb_2O_5 was pressed and sintered directly without any prior calcination. Single-phase $Zn_3Nb_2O_8$ ceramics could be obtained. Density of these ceramics increased with soaking time and sintering temperature. A maximum density 5.72 g/cm^3 (99.7% of the theoretical density) was found for pellets sintered at 1170 °C for 2 h. Pores were not found and grain sizes >20 μm were observed in pellets sintered at 1170 °C. Abnormal grain growth occurred and grains >50 μm could be seen in $Zn_3Nb_2O_8$ ceramics sintered at 1200 °C for 2 h and 1200 °C for 4 h. Reaction-sintering process is then a simple and effective method to produce $Zn_3Nb_2O_8$ ceramics for applications in microwave dielectric resonators.

Keywords: $Zn_3Nb_2O_8$; Dielectrics; 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 ceramics require a high relative permittivity (ε_r), a high quality factor (Q) and a small temperature coefficient of resonant frequency (τ_f). $ZnNb_2O_6$, $Zn_3Nb_2O_8$ and $Zn_2Nb_{34}O_{87}$ are phases which have been reported in the ZnO–Nb_2O_5 system [1,2]. $ZnNb_2O_6$ has the Columbite structure which can be interpreted as an ordered super-structure of α-PbO_2 [3]. The structure of $Zn_3Nb_2O_8$ is closely related to that of $ZnNb_2O_6$ [4]. $ZnNb_2O_6$ is often used as a precursor in the Columbite route to obtain single-phase perovskite $Pb(Zn_{1/3}Nb_{2/3})O_3$ or PZN-based materials for applications in multilayer ceramic capacitors and actuators [5,6]. Lee et al. reported that dense $Zn_3Nb_2O_8$ materials can be obtained with 2 mol% V_2O_5 addition after sintering at 850–1000 °C. $Zn_3Nb_2O_8$ ceramics with $\varepsilon_r = 22.4$ and $Q \times f = 67{,}500$ GHz were obtained [7]. Wu et al. lowered the sintering temperature of $Zn_3Nb_2O_8$ down to 950 °C by using 3 wt% of $0.29BaCO_3$–0.71CuO additives. The doped $Zn_3Nb_2O_8$ exhibits $\varepsilon_r = 14.7$ and $Q \times f = 8200$ GHz at 8.3 GHz [8]. Shlyakhtin and Oh [9] reported that $Zn_3Nb_2O_8$ powders with a grain size 50–300 nm were obtained by the thermal decomposition of freeze-dried Zn–Nb hydroxides or frozen oxalate solutions. The sintering of $Zn_3Nb_2O_8$ powders with CuO–V_2O_5 sintering aids resulted in $Zn_3Nb_2O_8$ ceramics with a relative density of 93–97%. $\varepsilon_r = 20$–21 and $Q \times f = 30{,}000$–36,000 GHz were obtained for sintering temperatures of 740–800 °C [9]. Kim et al. [10] obtained $Zn_3Nb_2O_8$ ceramics with $\varepsilon_r = 21.6$, $Q \times f = 83{,}300$ GHz and $\tau_f = -71$ ppm/°C. Materials with $\varepsilon_r = 36$, $Q \times f = 5190$ GHz and $\tau_f = 4$ ppm/°C were found in the system $(1-x)Zn_3Nb_2O_8$–$xTiO_2$ for $x = 0.725$.

Liou and co-workers have prepared microwave dielectric ceramics such as $BaTi_4O_9$, $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$, $(Pb,Ca)(Fe_{0.5}Nb_{0.5})_{1-x}Ti_xO_3$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $CaNb_2O_6$, $ZnNb_2O_6$, and $MgTiO_3$–$MgTi_2O_5$ using a reaction-sintering process [11–17]. Without any calcination step involved, the mixture of raw material powders was pressed and sintered directly into ceramics. This is a simple and effective method. $ZnNb_2O_6$ with a density 5.55 g/cm^3 (98.7% of T.D.) was obtained after sintering at 1180 °C for 4 h [16]. In this study, we tried to obtain $Zn_3Nb_2O_8$ ceramics via the reaction-sintering process.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: ZnO (99.6%, SHOWA, Japan) and Nb_2O_5 (99.8%,

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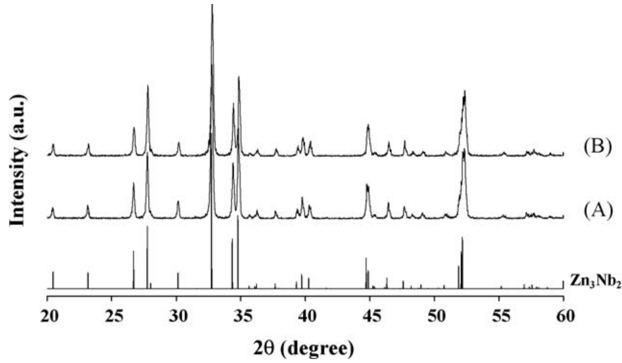

Fig. 1. The XRD patterns of $Zn_3Nb_2O_8$ ceramics sintered at (A) 1100 °C and (B) 1130 °C for 2 h.

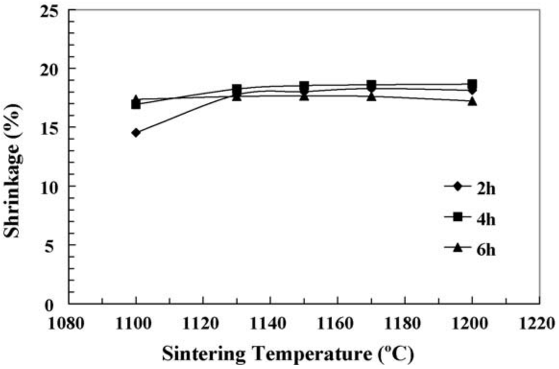

Fig. 2. Shrinkage percentages for $Zn_3Nb_2O_8$ ceramics sintered at various temperatures.

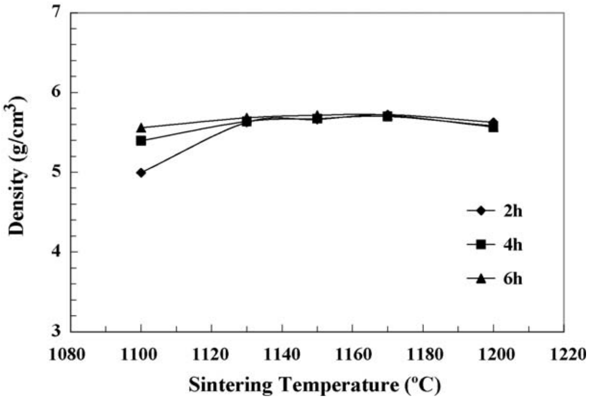

Fig. 3. Density values for $Zn_3Nb_2O_8$ ceramics sintered at various temperatures.

High Purity Chemicals, Japan). Appropriate amounts of raw materials were milled in acetone with zirconia balls for 12 h. After drying and pulverizing, the powder was uni-axially pressed into pellets of 12 mm in diameter and 1–2 mm thickness at a pressure of 100–150 MPa. The pellets were then heated at a rate of 10 °C/min and sintered in a covered alumina crucible at temperatures ranging from 1100 °C to 1200 °C for 2–6 h in air. Density of sintered pellets was measured using the Archimedes method. The sintered pellets were analyzed by X-ray diffraction (XRD) to check the nature of the phases present in the samples. Microstructures were observed by scanning electron microscopy (SEM).

3. Results and discussion

XRD patterns of $Zn_3Nb_2O_8$ ceramics sintered at 1100 °C and 1130 °C for 2 h are illustrated in Fig. 1. All reflections match with those of $Zn_3Nb_2O_8$ (JCPDS file no. 79-1164). It implies the reaction-sintering process is a simple and effective process to prepare single-phase $Zn_3Nb_2O_8$ ceramics even when the calcination stage was bypassed. Lee et al. found $ZnNb_2O_6$ phase during synthesis of $Zn_3Nb_2O_8$ after calcination at 900 °C

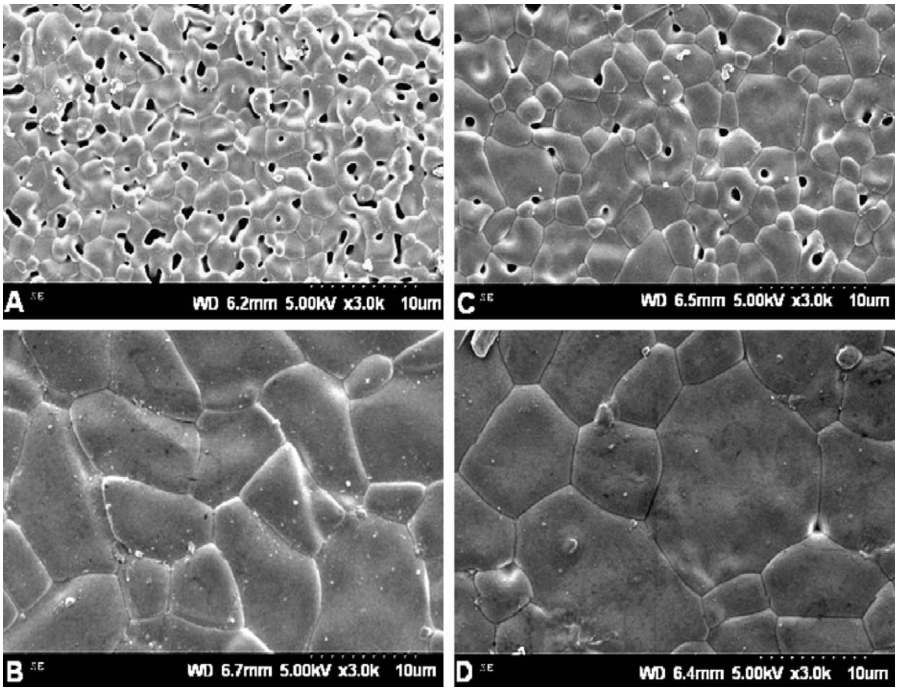

Fig. 4. SEM photos of as fired $Zn_3Nb_2O_8$ ceramics sintered at (A) 1100 °C/2 h, (B) 1170 °C/2 h, (C) 1100 °C/4 h, and (D) 1170 °C/4 h.

and 1000 °C for 2 h. Single-phase $Zn_3Nb_2O_8$ powder was obtained after calcining at 1100 °C for 2 h [7]. Wu et al. observed a phase of $ZnNb_2O_6$ containing ZnO formed after calcinations at 900 °C for 4 h during preparation of $Zn_3Nb_2O_8$ powder. A major phase of $ZnNb_2O_6$ combined with a secondary phase of $Zn_3Nb_2O_8$ was found in a powder calcined at 1000 °C for 4 h. A pure single phase of $Zn_3Nb_2O_8$ was formed only when the powder was calcined at 1100 °C [8]. Kim et al. obtained single phase $Zn_3Nb_2O_8$ ceramics after calcining at 1150 °C for 5 h and sintering at 1200 °C for 2 h [10]. Prasatkhetragarn et al. reported a single phase of $Zn_3Nb_2O_8$ formed in a powder calcined at 900–1100 °C for 5 h using solid-state mixed oxides via a rapid vibro-milling technique [18]. After comparison with these studies, reaction-sintering process appears as a simple and effective process to obtain $Zn_3Nb_2O_8$ ceramics. The calcination stage and rapid vibro-milling are not necessary.

The shrinkage percentage of $Zn_3Nb_2O_8$ sintered at 1100 °C for 2 h is only 14.5% indicating 2 h is not long enough for densification. It increases to 17–17.4% for 4 h and 6 h sintering at 1100 °C. Shrinkage percentage of 17.2–18.7% is observed for pellets sintered at 1130–1200 °C for 2–6 h as shown in Fig. 2. From the dilatometric curve, d'Astorg et al. reported a shrinkage percentage <12% in $Zn_3Nb_2O_8$ after calcining at 1100 °C/2 h and being heated to 1100 °C [19]. In our previous study, the shrinkage percentage of $ZnNb_2O_6$ reached 17.8% and 19.4% after sintering at 1100 °C/2 h and 1100 °C/4 h, respectively [20]. The variation of density in Fig. 3 shows similar trends to the variation observed for the shrinkage. A density of 5 g/cm^3 is observed for pellets sintered at 1100 °C for 2 h. Density increases with soaking time and sintering temperature. A maximum density 5.72 g/cm^3 (99.7% of T.D.) is found for pellets sintered at 1170 °C for 2 h. Lee et al. obtained $Zn_3Nb_2O_8$ ceramics of ~80% and ~96% of T.D. after sintering at 1000 °C/4 h and 1100 °C/4 h, respectively. Addition of 1 mol% V_2O_5 markedly enhances the densification and a density ~95% of T.D. is found for pellets sintered at 1000 °C/4 h. A density ~98% of T.D. is found for pellets containing 2 mol% V_2O_5 and sintered at 900 °C/4 h [7]. Wu et al. could get 92.7% of T.D. after calcination at 1100 °C/4 h and sintering at 1150 °C/4 h. With 3 wt% $0.21BaCO_3$–$0.79CuO$ addition, they obtained 92.1% and 96.1% of T.D. after sintering at 950 °C/4 h and 1050 °C/4 h, respectively. With 3 wt% $0.81MoO_3$–$0.19CuO$ addition, they found 93.5% and 95.1% of T.D. after sintering at 950 °C/4 h and 1000 °C/4 h, respectively [8]. Shlyakhtin and Oh reported a density 93–97% of T.D. for $Zn_3Nb_2O_8$ ceramics containing CuO–V_2O_5 sintering aids and sintered at 740–800 °C by using the thermal decomposition of freeze-dried Zn–Nb hydroxides or frozen oxalate solutions [9]. After comparison with these results, reaction-sintering process proves to be a simple and effective process to obtain highly dense $Zn_3Nb_2O_8$ ceramics even without the calcination stage and without any addition of sintering aids.

SEM photos of as fired $Zn_3Nb_2O_8$ ceramics are shown in Fig. 4. Porous pellet with grains less than 4 μm could be seen in $Zn_3Nb_2O_8$ sintered at 1100 °C/2 h. The amount of pores decreased and grains of 8 μm could be seen in $Zn_3Nb_2O_8$ sintered at 1100 °C/4 h. This is in agreement with variations of shrinkage and density reported in Figs. 2 and 3. Pores are not found and grains >20 μm exist in pellets sintered at 1170 °C. Huang et al. observed abnormal grain growth in $Zn_3Nb_2O_8$ ceramics. Grains >100 μm could be seen in $Zn_3Nb_2O_8$ calcined at 1050 °C/2 h and sintered at 1200 °C/4 h [21]. Abnormal grain growth is also observed in this study. Grains >50 μm could be seen in $Zn_3Nb_2O_8$ sintered at 1200 °C/2 h and 1200 °C/4 h as shown in Fig. 5. In our previous study, 0.9–6.9 μm grains were formed in $ZnNb_2O_6$ pellets sintered at 1100–1250 °C for 2 h and 4 h via reaction-sintering process [16]. Therefore, grain growth is easier in $Zn_3Nb_2O_8$ than in $ZnNb_2O_6$ prepared using reaction-sintering process.

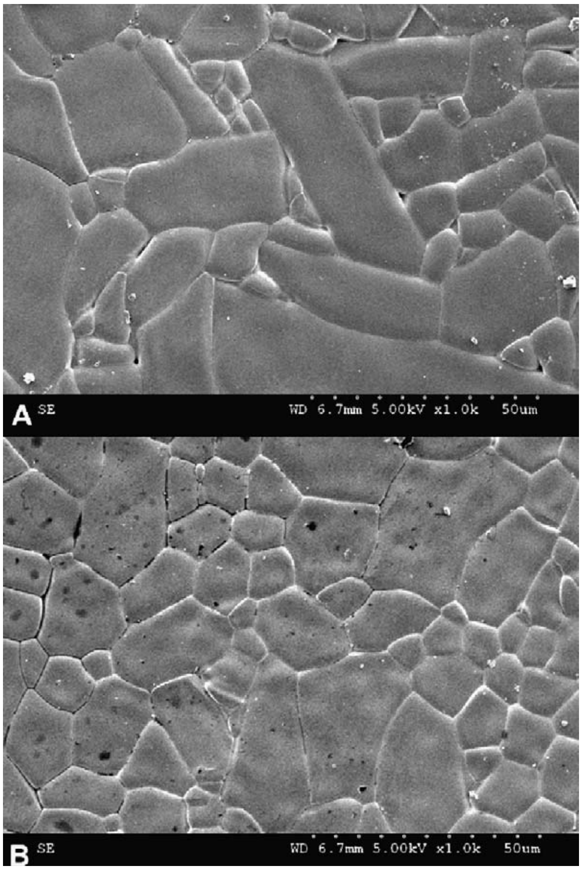

Fig. 5. SEM photos of as fired $Zn_3Nb_2O_8$ ceramics sintered at (A) 1200 °C/2 h, and (B) 1200 °C/4 h.

4. Conclusion

Reaction-sintering process can transform a mixture of ZnO and Nb_2O_5 into single-phase $Zn_3Nb_2O_8$ ceramic even when the calcination stage is bypassed. Density increases with soaking time and sintering temperature. A maximum density 5.72 g/cm^3 (99.7% of the theoretical density) was achieved for pellets sintered at 1170 °C for 2 h. Pores were not found and grain size >20 μm formed in pellets sintered at 1170 °C. Abnormal grain growth is observed and grains >50 μm could be seen in $Zn_3Nb_2O_8$ sintered at 1200 °C/2 h and 1200 °C/4 h. Reaction-sintering process is a simple and effective method to produce $Zn_3Nb_2O_8$ ceramics for applications in microwave dielectric resonators.

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