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Low-temperature synthesis of $BiNbO_4$ ceramics using reaction-sintering process

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Abstract

Low-temperature synthesis of $BiNbO_4$ ceramics using reaction-sintering process was investigated. Orthorhombic $BiNbO_4$ phase together with minor triclinic $BiNbO_4$ phase were found in the pellets. The phase transition temperature in $BiNbO_4$ with 0.5 wt% CuO addition was lowered from 960 °C via traditional route to 880 °C when the reaction-sintering process was used. After 920 °C sintering for 4 and 6 h, densities 6.8–6.85 g/cm^3 (94% of the theoretical value) were obtained. The abnormal grain growth in $BiNbO_4$ via traditional route was not observed in this study.

Keywords: $BiNbO_4$; CuO; Reaction-sintering process

1. Introduction

Microwave dielectrics have been widely investigated for the use of resonators and filters in the satellite and mobile communication systems. Complex perovskite compounds such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) exhibit excellent microwave dielectric properties [1,2]. However, fairly high sintering temperatures (>1400 °C) are needed to obtain these oxide compounds ceramics. They are not suitable to be used in multilayered microwave devices via low-temperature co-fired ceramic (LTCC) technology. Low firing microwave dielectrics are needed in order to use low-melting point conductors such as silver and copper. $BiNbO_4$ ceramics have been found with a low sintering temperature. Kagata and co-workers first reported the microwave properties of $BiNbO_4$ ceramics. Dense $BiNbO_4$ ceramics were difficult to obtain without addition of low-melting oxide. Dense $BiNbO_4$ ceramics could be obtained with V_2O_5 or CuO addition. They found $\varepsilon_r \sim 43$, $Q \times f = 10{,}000$–$17{,}000$ GHz. $\tau_f > 0$ ppm/°C with V_2O_5 addition and <0 ppm/°C with CuO addition were observed while $\tau_f \sim 0$ ppm/°C could be obtained by CuO–V_2O_5 addition together [3]. Cheng et al. obtained $BiNbO_4$ ceramics with 0.5 wt% CuO addition with properties: $\varepsilon_r = 43.6$, $Q \times f = 10070$ GHz (6.25 GHz) and $\tau_f = -20.8$ ppm/°C after calcining at 800 °C/3 h and sintering at 920 °C/4 h [4]. Huang et al. obtained $BiNbO_4$ ceramics with 0.5 wt% CuO addition with properties: $\varepsilon_r = 43.3$, $Q \times f = 13{,}000$ GHz (6.3 GHz) and $\tau_f = 15$ ppm/°C after calcining at 800 °C/3 h and sintering at 900 °C/3 h [5].

Recently, Liou and co-workers 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 reaction-sintering process [6–12]. With the calcination step bypassed, the mixture of raw material powders was pressed and sintered directly into ceramics. It is a simple and effective method. In this study, authors try to obtain $BiNbO_4$ ceramics via the reaction-sintering process.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: Bi_2O_3 (99.7%, Showa, Japan), Nb_2O_5 (99.8%, High purity chemicals, Japan) and CuO (99%, Showa, Japan). Appropriate amounts of raw materials for stoichiometric $BiNbO_4$ were weighted with 0.5 wt% CuO addition 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 a covered alumina

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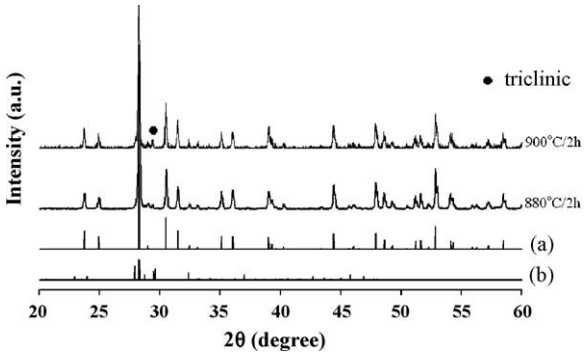

Fig. 1. XRD profiles of $BiNbO_4$ ceramics sintered at 880 °C and 900 °C for 2 h.

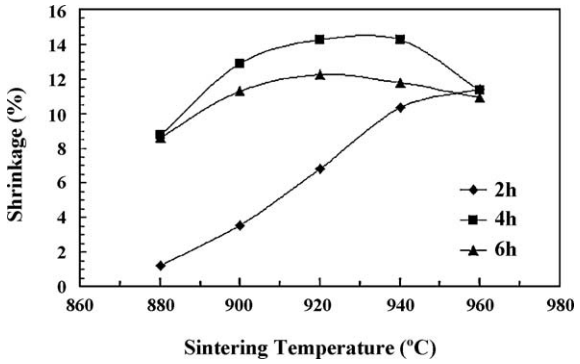

Fig. 2. Shrinkage percentage of $BiNbO_4$ ceramics sintered at various temperatures and soak time.

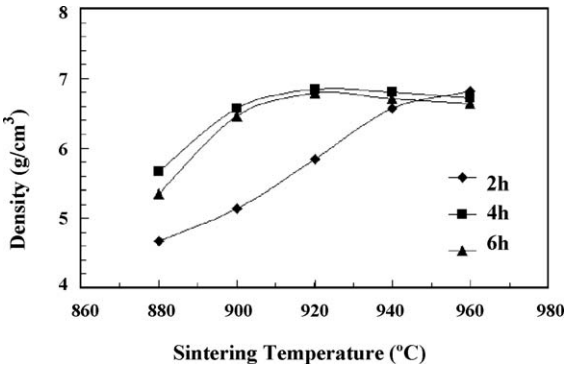

Fig. 3. Density of $BiNbO_4$ ceramics sintered at various temperatures and soak time.

crucible at temperatures ranging from 880 to 960 °C for 2–6 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

Fig. 1 shows the XRD profiles of $BiNbO_4$ ceramics sintered at 880 °C and 900 °C for 2 h. Orthorhombic $BiNbO_4$ (JCPDS file no. 82-0348) phase together with minor triclinic $BiNbO_4$ (ICDD #00-016-0486) phase were found in the pellets. This proves the $BiNbO_4$ phase 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 $BiNbO_4$ ceramics. $BiNbO_4$ has two polymorph phases, low-temperature orthorhombic α-phase and high temperature triclinic β-phase. Pure α-$BiNbO_4$ has a crystal structure of the orthorhombic-$SbTaO_4$ type below 1020 °C, and transform to β-phase when the temperature increases [13,14]. The phase transition temperature in $BiNbO_4$ could be lowered as CuO is added. Cheng et al. reported that β-phase was not found in $BiNbO_4$ pellets with 0–0.5 wt% CuO addition after calcining at 800 °C/3 h and sintering at 920 °C/4 h. As 1 wt% CuO was added, minor β-phase was found [4]. Huang et al. obtained single α-phase $BiNbO_4$ ceramics with 0.5 wt% CuO added after calcining at 800 °C/3 h and sintering at 880–920 °C/3 h. Minor β-phase was found in $BiNbO_4$ pellets sintered at 960 °C/3 h [5]. The phase transition temperature in $BiNbO_4$ with 0.5 wt% CuO addition seems to be further lowered to 880 °C in this study when the reaction-sintering process was used.

The shrinkage percentage of $BiNbO_4$ pellet is low for 2 h sintering at 880–920 °C as shown in Fig. 2. For 4 and 6 h sintering, it increases from 8.6% at 880 °C to 12.3–14.3% at 920 °C. It indicates a full sintering occurred at 900–940 °C/4–6 h. In Fig. 3, the density of $BiNbO_4$ pellet is low for 2 h sintering at 880–920 °C. For 4 and 6 h sintering, it increases from 5.3–5.7 g/cm^3 at 880 °C to 6.8–6.85 g/cm^3 (94% of the theoretical value 7.28) at 920 °C. Cheng et al. reported $BiNbO_4$ ceramics with 0.125 and 0.25 wt% CuO, a bulk density of around 96.6 and 98.6% of the theoretical density can be obtained at 960 and 940 °C, respectively. As the CuO amount is in the range of 0.5–1.0 wt%, the $BiNbO_4$ ceramics could be densified at 900–920 °C [4]. Huang et al. obtained a maximum density 7.11 g/cm^3 (97.7% of the theoretical value 7.28) in $BiNbO_4$ ceramics with 0.5 wt% CuO added after calcining at 800 °C/3 h and sintering at 900 °C/3 h [5]. In our previous studies, highly dense (97–99% of the theoretical value) ceramics such as $BaTi_4O_9$, $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$, $(Pb,Ca)(Fe_{0.5}Nb_{0.5})_{1-x}Ti_xO_3$, $Ba_5Nb_4O_{15}$, $ZnNb_2O_6$, and $NiNb_2O_6$ could be prepared using reaction-sintering process [6–9,11,15]. Density of $BiNbO_4$ via reaction-sintering process in this study is lower than those via traditional oxide route. A low sintering temperature below 960 °C is the main reason. It is more difficult to obtain dense ceramics without calcining the mixture of raw powers before the sintering stage.

The SEM photos of $BiNbO_4$ ceramics sintered at 900–960 °C for 2 h are shown in Fig. 4. Porous pellets with small grains less than 4 μm are seen in $BiNbO_4$ ceramics sintered at 900 °C and this resulted in a low density 5.14 g/cm^3. Pores decreased and grain growth increased in pellets sintered at higher sintering temperatures. Grains >10 μm could be found in $BiNbO_4$ ceramics sintered at 940 °C and this resulted in a high density 6.57 g/cm^3. Almost no pores are observed in 960 °C sintering pellets. Pores decrease and larger grains are found in pellets sintered for 4 and 6 h as shown in Figs. 5 and 6. This may explain

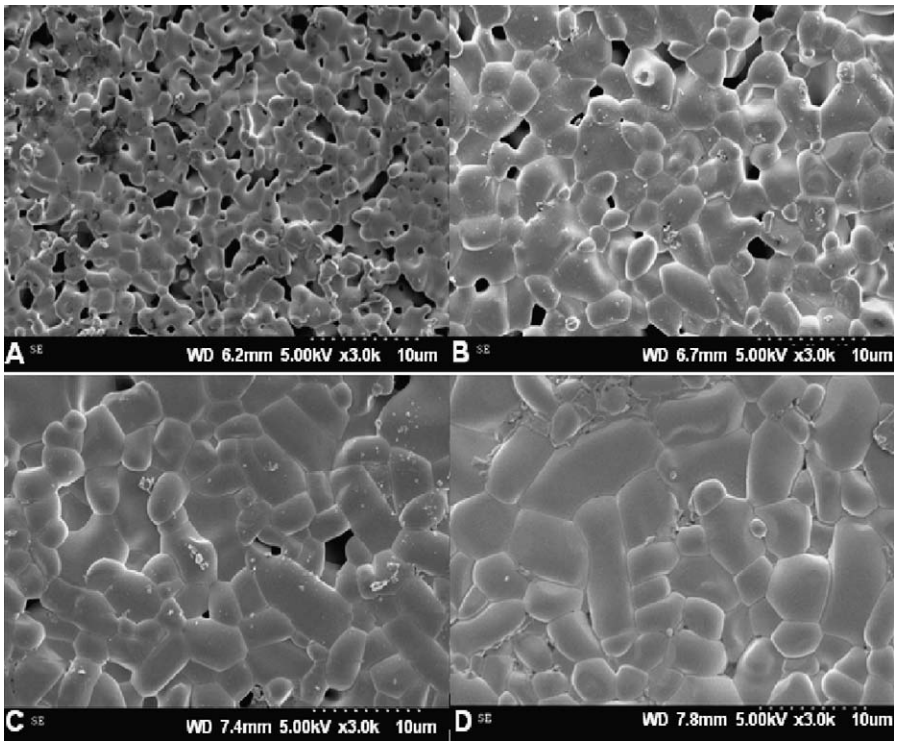

Fig. 4. SEM photographs of as-fired $BiNbO_4$ ceramics sintered at (A) 900 °C, (B) 920 °C, (C) 940 °C and (D) 960 °C for 2 h.

why the shrinkage and density for 4 and 6 h sintering pellets are higher than the 2 h sintering pellets. Cheng et al. obtained grains <10 μm in $BiNbO_4$ ceramics with 0.5 wt% CuO addition after calcining at 800 °C/3 h and sintering at 920 °C/4 h [4]. Huang et al. obtained grains <10 μm in $BiNbO_4$ ceramics with 0.5 wt% CuO addition after calcining at 800 °C/3 h and sintering at 920 °C/3 h. Abnormal grain growth (>50 μm) was observed in $BiNbO_4$ ceramics with 0.5 wt% CuO addition after sintering at 960 °C/3 h and 920 °C/6 h [5]. In this study, the abnormal grain growth was not observed.

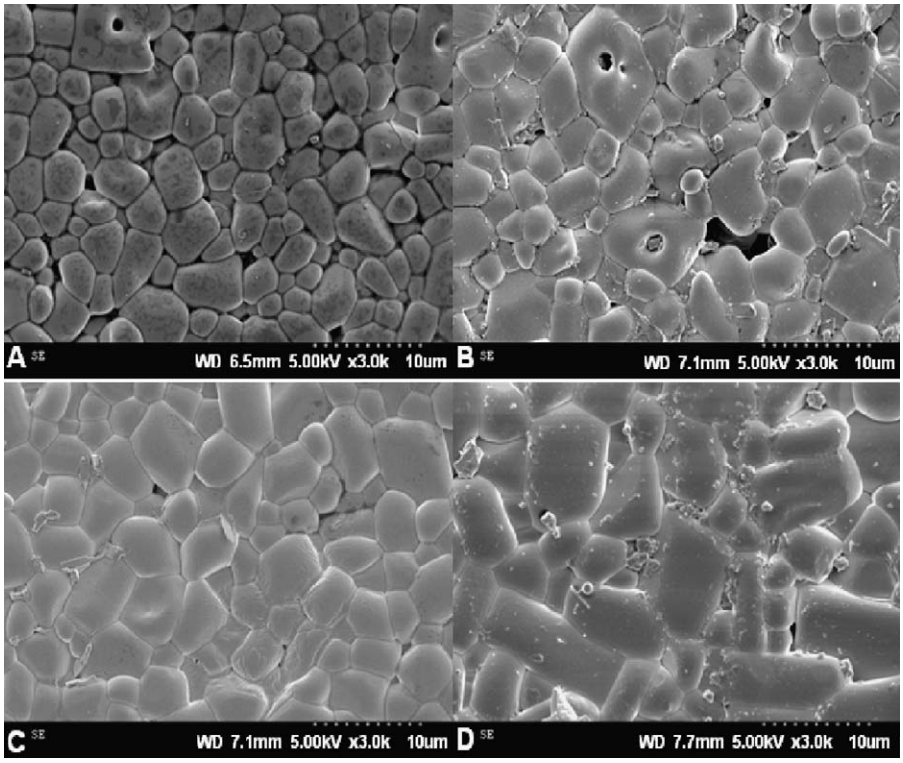

Fig. 5. SEM photographs of as-fired $BiNbO_4$ ceramics sintered at (A) 900 °C, (B) 920 °C, (C) 940 °C and (D) 960 °C for 4 h.

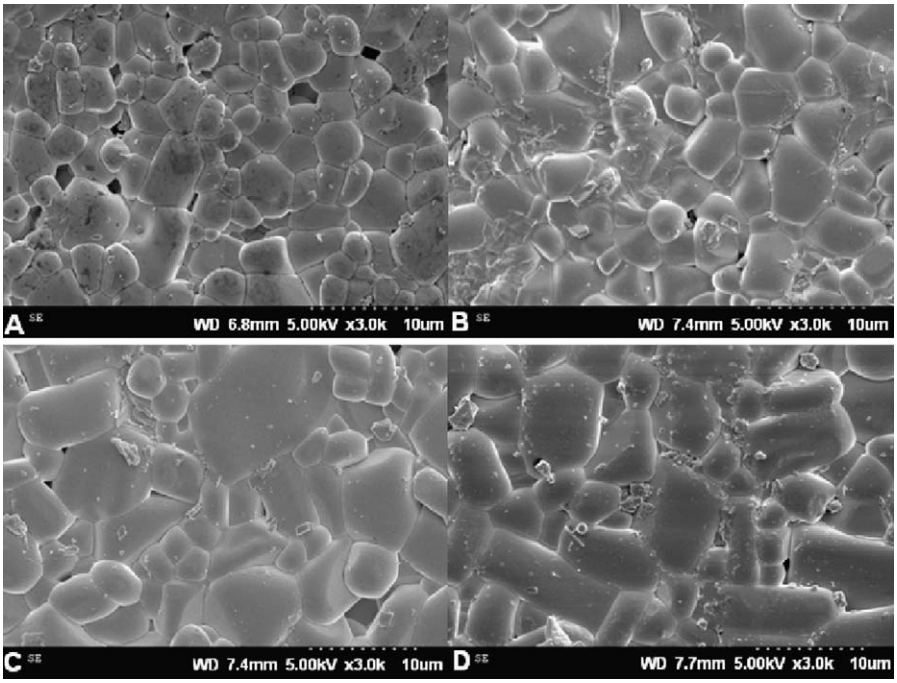

Fig. 6. SEM photographs of as-fired $BiNbO_4$ ceramics sintered at (A) 900 °C, (B) 920 °C, (C) 940 °C and (D) 960 °C for 6 h.

4. Conclusions

$BiNbO_4$ ceramics were obtained successfully via a reaction-sintering process. Orthorhombic $BiNbO_4$ phase together with minor triclinic $BiNbO_4$ phase were found in the pellets. The phase transition temperature in $BiNbO_4$ with 0.5 wt% CuO addition was lowered from 960 °C via traditional route to 880 °C when the reaction-sintering process was used. After 920 °C sintering for 4 and 6 h, densities 6.8–6.85 g/cm^3 (94% of the theoretical value) were obtained. The abnormal grain growth in $BiNbO_4$ via traditional route was not observed.

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