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Synthesis and properties of $Ba_2La_3Ti_3NbO_{15}$ ceramics by a reaction-sintering process

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Abstract

Synthesis of $Ba_2La_3Ti_3NbO_{15}$ (BLTN) microwave ceramics by a simple and effective reaction-sintering process was investigated. The mixture of $BaCO_3$, La_2O_3, TiO_2 and Nb_2O_5 was pressed and sintered directly without any calcinations involved. BLTN ceramics could be obtained after 2–6 h sintering at 1430–1500 °C. A density 6.08 g/cm^3 (98% of the theoretical value) after sintering at 1500 °C for 6 h. $\varepsilon_r = 47$ and $Qf \sim 2000$ GHz and a τ_f value ~+20 ppm/°C were obtained in BLTN ceramic sintered at 1470 °C/6 h.

Keywords: $Ba_2La_3Ti_3NbO_{15}$; Dielectrics; Reaction-sintering process

1. Introduction

Dielectric resonators used in microwave frequency have been widely investigated due to the fast growth of satellite and mobile communication systems. Microwave dielectric materials require a high relative permittivity (ε_r), a high quality factor (Q) and a small temperature coefficient of resonant frequency (τ_f). Galasso and Katz had first investigated hexagonal perovskite ceramics $A_5Ta_4O_{15}$ (A = Ba or Sr) and $Ba_5Nb_4O_{15}$ [1]. Sreemoolanadhan et al. investigated microwave properties of $Ba_5Nb_4O_{15}$ and found it exhibited superior dielectric properties for resonator applications [2,3]. Vineis et al. obtained $Ba_5Nb_4O_{15}$ with $\varepsilon_r = 39.3$, $Qf = 26{,}337$ GHz and $\tau_f = 79.1$ ppm/°C [4]. Fang et al. reported a new hexagonal perovskite ceramic $Ba_2La_3Ti_3NbO_{15}$ with properties: $\varepsilon_r = 42.83$, $Qf = 21{,}726$ GHz (5.8562 GHz) and $\tau_f = -8$ ppm/°C [5].

Recently, a simple and effective reaction-sintering process was reported by Liou and co-workers in producing $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) ceramics [6–11]. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics with the calcinations step in the traditional oxide route bypassed. PMN ceramics with a density of 8.09 g/cm^3 (99.5% of the theoretical value) and high relative permittivity 19,900 (1 kHz) were obtained. This reaction-sintering process had also been used to produce other complex perovskite relaxor ceramics successfully. In the recent studies, we also prepared dense and pure phased $BaTi_4O_9$ and $CaNb_2O_6$ ceramics by this process successfully [12,13]. In this study, the authors try to obtain $Ba_2La_3Ti_3NbO_{15}$ ceramics by the reaction-sintering process.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: $BaCO_3$ (J.T. Baker, 99.8%), La_2O_3 (SHOWA, 99.99%), TiO_2 (SHOWA, 99.99%) and Nb_2O_5 (High Purity Chemicals, 99.9%). Appropriate amounts of raw materials for $Ba_2La_3Ti_3NbO_{15}$ (BLTN) were milled in acetone with zirconia balls for 12 h at a speed 450 rpm. After drying and pulverizing, the powder was uni-axially pressed into pellets of 12 mm in diameter and 2–3 mm thick (6–7 mm thick for microwave properties measurement) at a pressure of 100–150 MPa. The pellets were then heated at a rate 10 °C/min and sintered in covered alumina crucible at temperatures ranging from 1430 °C to 1500 °C for 2–6 h in air. Density of sintered pellets was measured using the Archimedes method. The sintered pellets were analyzed by the X-ray diffraction (XRD) to check the

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reflections of the phases. Microstructures were analyzed by scanning electron microscopy (SEM). Relative permittivity at a frequency range 10 kHz to 10 MHz was measured with the Agilent 4294A impedance analyzer. The relative permittivity at microwave frequency was calculated by the size of sample and the frequency of TE_{011} mode using the Hakki–Coleman dielectric resonator method [14]. The temperature coefficient of resonant frequency (τ_f) at microwave frequency was measured in the temperature range from 25 °C to 85 °C, and calculated by 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 $TE_{01\delta}$ resonant frequency at 85 °C and 25 °C, respectively. 8720ES network analyzer (Agilent) was employed in the measurement.

3. Results and discussion

Fig. 1 shows the XRD patterns of BLTN ceramics produced using the reaction-sintering process. In BLTN ceramics Fang et al. prepared, the mixtures were calcined in the range 1300–1350 °C for 4 h and sintered at 1460 °C for 4 h [5]. In this study, there were 13–15 min to heat from 1300 °C to 1430–1450 °C at a rate 10 °C/min. Calcination reaction happened during the heating up period, reactants reacted and transformed into BLTN phase. All reflections match with those of BLTN ceramics investigated by Fang et al. [5]. This implies the reaction-sintering process is a simple and effective process to prepare BLTN ceramics even the calcination stage was bypassed. The shrinkage percentage for BLTN pellet for 2 h sintering increases almost linearly with sintering temperature. For 4 h and 6 h sintering, it increases from 1430 °C and saturates at temperatures above 1470 °C as shown in Fig. 2. It indicates the sintering temperature to enable maximum density occurred at 1470 °C. The sintering temperature to enable maximum density of $Ba_5Nb_4O_{15}$ prepared by the reaction-sintering process occurred at 1450 °C [15]. It implies the temperature for densification in BLTN is higher than in $Ba_5Nb_4O_{15}$. In Fig. 3, the density value of BLTN ceramics increases with sintering temperature and reaches a maximum value 5.94 g/cm^3 and 6.08 g/cm^3 (98% of the theoretical value) after sintering at 1500 °C for 4 h and 6 h, respectively. In the study of Fang et al., 96.8% of the theoretical value was obtained in BLTN ceramics after calcined at 1300–1350 °C for 4 h and sintered at 1460 °C for 4 h [5]. The major difference between reaction-sintering process and other processes is that the particles in the pressed pellets to be 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 more pores between clusters and result in lower shrinkage during sintering. While in reaction-sintering process, particles begin to react with each other then the nucleation occurs and the pellet is entirely agglomerated. Therefore, the reaction-sintering process is effective to produce BLTN ceramics with high density even without the calcination stage and the addition of sintering aid.

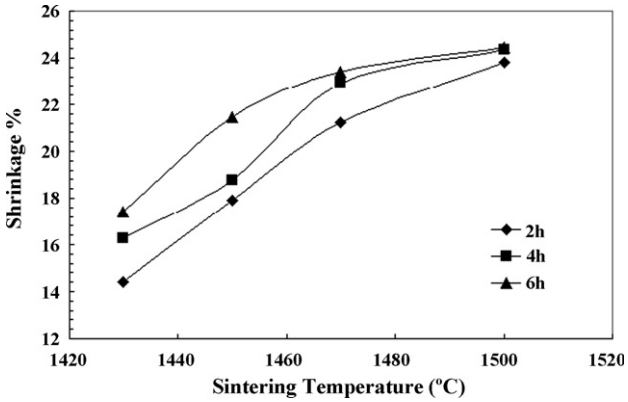

Fig. 2. Shrinkage percentages for BLTN ceramics sintered at various temperatures.

SEM photos of as fired BLTN ceramics are shown in Figs. 4 and 5. Grain growth was not obvious at 1430 °C and 1450 °C. The amount of pores decreased and grain size increased at temperatures above 1470 °C. It is in good agreement with the shrinkage and density values in Figs. 2 and 3. Microstructure morphology similar to those observed in BLTN ceramics reported by Fang et al. [5] was observed. Relative permittivity measured in a frequency range 10 kHz to 10 MHz for BLTN ceramics sintered at 1470 °C were shown in Fig. 6. At 10 MHz, values increased from 38.5 to 43 as the sintering time increased

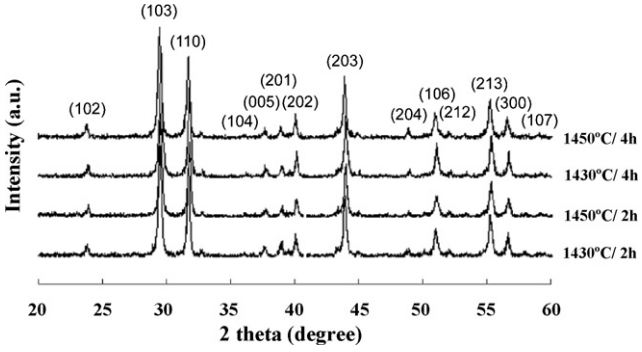

Fig. 1. The XRD patterns of BLTN ceramics.

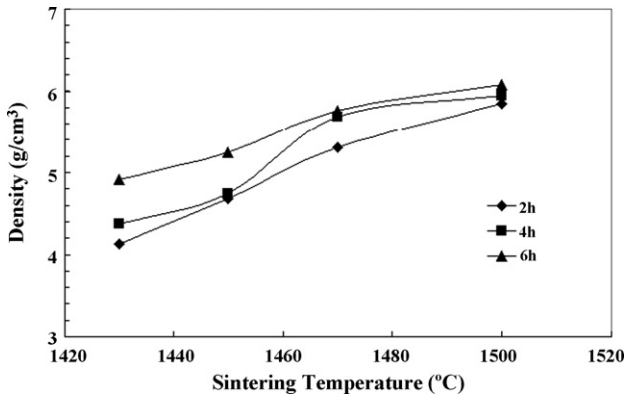

Fig. 3. Density values for BLTN ceramics sintered at various temperatures.

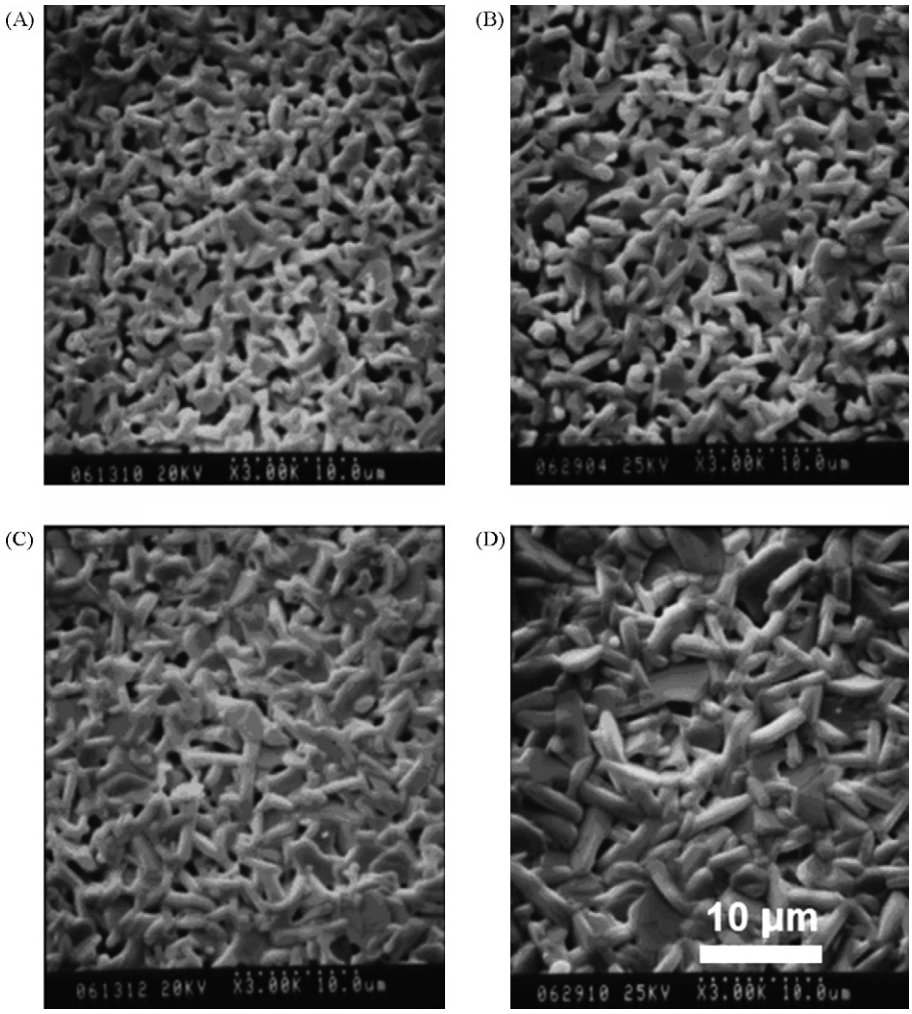

Fig. 4. SEM photos of as fired BLTN ceramics sintered at (A) 1430 °C, (B) 1450 °C, (C) 1470 °C and (D) 1500 °C for 2 h.

from 2 h to 6 h due to the increased density and grain size. Relative permittivity of 43.9 at 1 MHz for BLTN ceramics produced using conventional solid state ceramic route was measured in the study of Fang et al. [5]. Dielectric properties of BLTN ceramics at microwave frequency via various processes are listed in Table 1. $\varepsilon_r = 47$ and $Qf \sim 2000$ GHz and a τ_f value ~+20 ppm/°C were obtained in BLTN ceramic sintered at 1470 °C/6 h. In the studies of Fang et al. BLTN ceramics with $\varepsilon_r = 42.84$, $Qf \sim 21{,}726$ GHz and $\tau_f = -8$ ppm/°C were obtained [5]. Higher ε_r was resulted from a higher density. The much lower Qf may be caused by the formation of micro-cracks in the pellets during sintering as we did not add any binder into the mixture of raw materials. Similar results were obtained in $Ba_3La_2Ti_2Nb_2O_{15}$ ceramics prepared using a reaction-sintering process. We obtained properties: $\varepsilon_r = 51.5$–54.5, $Qf < 8000$ GHz and $\tau_f < +15$ ppm/°C [16]. In the studies of Fang et al. $Ba_3La_2Ti_2Nb_2O_{15}$ ceramics with $\varepsilon_r = 49.37$, $Qf \sim 20{,}207$ GHz and $\tau_f = +4$ ppm/°C were obtained [5]. From the results discussed above, the reaction-sintering process has been proven a simple and effective method to produce dense BLTN ceramics with high ε_r even without the addition of sintering aid. Modification of process parameters to increase Qf value by adding PVA binder or sintering aid such as B_2O_3 are still under investigation.

Table 1
Microwave properties of BLTN ceramics prepared by various methods

Proposed by	Fang et al. [5]	This work
Processing	Conventional solid oxide route	Reaction-sintering process
Calcination temperature	1300–1350 °C/4 h	No calcining
Sintering temperature/time	1460 °C/4 h (PVA binder)	1470 °C/6 h (no binder added)
ε_r	42.83	47
Qf (GHz)	21,726	~2000
τ_f (ppm/°C)	−8	~+20

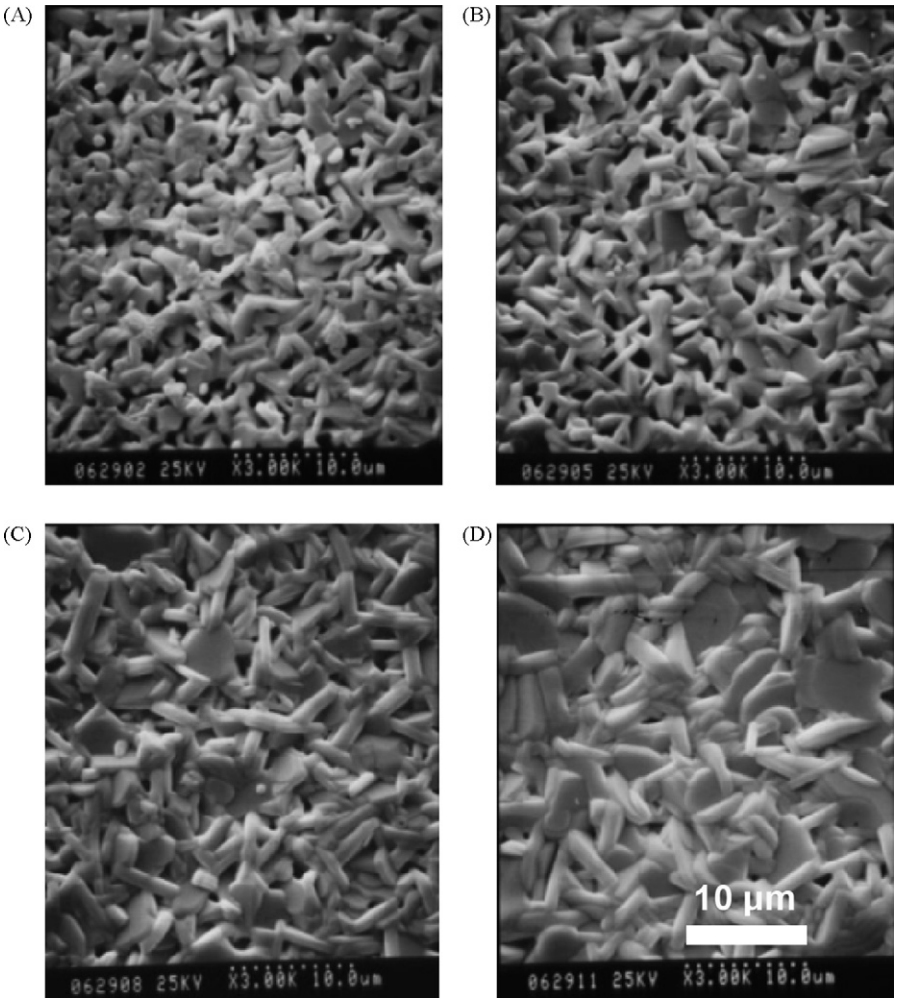

Fig. 5. SEM photos of as fired BLTN ceramics sintered at (A) 1430 °C, (B) 1450 °C, (C) 1470 °C and (D) 1500 °C for 4 h.

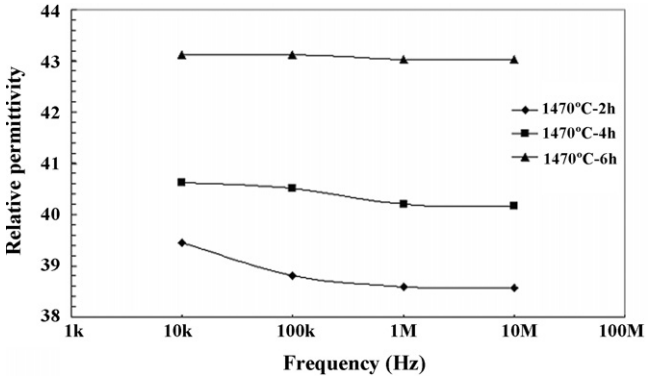

Fig. 6. Relative permittivity of BLTN sintered at 1470 °C for 2–6 h.

4. Conclusion

Reaction-sintering process could transform the mixture of $BaCO_3$, La_2O_3, TiO_2 and Nb_2O_5 into $Ba_2La_3Ti_3NbO_{15}$ ceramic even the calcination stage is bypassed. Density of BLTN ceramic increases with sintering temperature and reaches a maximum value 6.08 g/cm^3 (98% of the theoretical value) after sintering at 1500 °C for 6 h. $\varepsilon_r = 47$ and $Qf \sim 2000$ GHz and a τ_f value ~+20 ppm/°C were obtained in BLTN ceramic sintered at 1470 °C/6 h. Reaction-sintering process is a simple and effective method to produce $Ba_2La_3Ti_3NbO_{15}$ ceramics for applications in microwave dielectric resonators.

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References

[1] F. Galasso, L. Katz, Preparation and structure of $Ba_5Ta_4O_{15}$ and related compounds, Acta Crystallogr. 14 (1961) 647–650.
[2] H. Sreemoolanadhan, J. Isaac, S. Solomon, M.T. Sebastian, K.A. Jose, P. Mohanan, Dielectric properties of $Ba_5Nb_4O_{15}$ ceramics, Phys. Stat. Sol. 143 (1994) K45–K48.
[3] H. Sreemoolanadhan, M.T. Sebastian, P. Mohanan, High permittivity and low loss ceramics in the BaO–SrO–Nb_2O_5 system, Mater. Res. Bull. 30 (6) (1995) 653–658.

[4] C. Vineis, P.K. Davis, T. Negas, S. Bell, Microwave dielectric properties of hexagonal perovskites, Mater. Res. Bull. 31 (5) (1996) 431–437.
[5] L. Fang, H. Zhang, X.K. Hong, F.C. Meng, J.F. Yang, T.H. Huang, Preparation and characterization of two new dielectric ceramics $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$, Mater. Lett. 58 (2004) 3884–3887.
[6] Y.-C. Liou, K.H. Tseng, C.H. Yu, $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics produced by reaction-sintering process, in: Proceedings of the 2001 Annual Conference of the Chinese Society for Materials Science, November 23–24, National Chung Hsing University, Taichung, Taiwan, 2001, pp. 03–09.
[7] Y.-C. Liou, K.H. Tseng, C.H. Yu, Stoichiometric PMN–PT ceramics produced by reaction-sintering process, in: Proceedings of the 2001 Annual Conference of the Chinese Society for Materials Science, November 23–24, National Chung Hsing University, Taichung, Taiwan, 2001 pp. 03–17.
[8] Y.-C. Liou, C.Y. Shih, C.H. Yu, $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics produced by reaction-sintering process, in: Proceedings of the 2001 Annual Conference of the Chinese Society for Materials Science, November 23–24, National Chung Hsing University, Taichung, Taiwan, 2001, pp. 03–102.
[9] Y.-C. Liou, K.H. Tseng, Stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ perovskite ceramics produced by reaction-sintering process, Mater. Res. Bull. 38 (8) (2003) 1351–1357.
[10] Y.-C. Liou, C.Y. Shih, C.H. Yu, Stoichiometric $Pb(Fe_{1/2}Nb_{1/2})O_3$ perovskite ceramics produced by reaction-sintering process, Mater. Lett. 57 (2003) 1977–1981.
[11] Y.-C. Liou, Stoichiometric perovskite PMN–PT ceramics produced by reaction-sintering process, Mater. Sci. Eng. B 103 (3) (2003) 281–284.
[12] Y.-C. Liou, C.T. Wu, K.H. Tseng, T.C. Chung, Synthesis of $BaTi_4O_9$ ceramics by reaction-sintering process, Mater. Res. Bull. 40 (9) (2005) 1483–1489.
[13] Y.-C. Liou, M.H. Weng, C.Y. Shiue, $CaNb_2O_6$ ceramics prepared by a reaction-sintering process, Mater. Sci. Eng. B 133 (2006) 14–19.
[14] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IRE Trans. Microwave Theory Tech. MTT-8 (1960) 402–410.
[15] Y.-C. Liou, W.H. Shiu, C.Y. Shih, Microwave ceramics $Ba_5Nb_4O_{15}$ and $Sr_5Nb_4O_{15}$ prepared by a reaction-sintering process, Mater. Sci. Eng. B 131 (2006) 142–146.
[16] Y.-C. Liou, C.-Y. Liu, A simple and effective process for $Ba_3La_2Ti_2Nb_2O_{15}$ microwave ceramics, Mater. Sci. Eng. A 448 (2007) 351–355.