



Densification, microstructural evolution, and dielectric properties of hexagonal Ba(Ti_{1-x}Mn_x)O₃ ceramics sintered with fluxes

Sea-Fue Wang*, Yuh-Ruey Wang, Yu-Chuan Wu, Yu-Jung Liu

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei 106, Taiwan, ROC

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ABSTRACT

Recently, doped hexagonal BaTiO₃ (6h-BaTiO₃) ceramics have been reported as potential candidates used in microwave dielectric resonators. However, similar to other common microwave ceramics, doped 6h-BaTiO₃ ceramics require a high sintering temperature, greater than 1300 °C. In this study, the effect of sintering aids, including Bi₂O₃, B₂O₃, BaSiO₃, Li₂CO₃, CuO, V₂O₅, 5ZnO·2B₂O₃, and 5ZnO·2SiO₂, on the densification, microstructural evolution, and microwave properties of the 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics was examined. Results indicate that among the fluxes studied, Bi₂O₃, B₂O₃, and Li₂CO₃ could effectively reduce the sintering temperature of 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics through liquid phase sintering, while retaining the hexagonal structure and the microwave dielectric properties. The best results were obtained for the 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ with the additions of 5 wt% Bi₂O₃ sintered at 900 °C (ϵ_r : 54.7, Q_f : 1323, and τ_f : 183.3 ppm/°C), 10 wt% B₂O₃ sintered at 1100 °C (ϵ_r : 54.4, Q_f : 3448, and τ_f : 254.5 ppm/°C), and 5 wt% Li₂CO₃ sintered at 950 °C (ϵ_r : 43.7, Q_f : 2501, and τ_f : -29.8 ppm/°C).

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1. Introduction

Barium titanate, BaTiO₃, based ceramics, which are commonly recognized as cornerstone of electroceramics, find applications in capacitors, positive temperature coefficient of resistance (PTCR) thermistors, chemical sensors, and piezoelectric devices. Most research to date has focused on the low-temperature tetragonal polymorph (t-BaTiO₃), due to the fact that it possesses the ferroelectric properties and the high dielectric constant at room temperature ($\epsilon_r \approx 1000$ –2000). Hexagonal BaTiO₃ (6h-BaTiO₃) polymorph is reported to be thermodynamically stable above 1460 °C according to the BaO–TiO₂ phase diagram [1]. Yet, it is kinetically stabilized at room temperature by many routes such as rapid quenching to room temperature after sintering at >1460 °C in air [1], or sintering at above 1300 °C in reducing atmosphere [2,3], and also by sintering of acceptor-doped BaTiO₃ in air [4–6]. For the latter two routes, the formation temperature of the 6h-BaTiO₃ is well below the h → c phase transformation temperature, 1460 °C [5].

Recently, doped 6h-BaTiO₃ ceramics were reported as potential candidates for use in dielectric resonators [6–9]. Wang et al. [8,9] investigated the microwave properties of doped 6h-BaTiO₃ ceramics and found that the best results were obtained for the

composition of 6h-Ba(Ti_{0.65}Mn_{0.35})O₃ (ϵ_r : 41.2, Q_f : 14300, and τ_f : 18.6 ppm/°C). However, similar to common microwave ceramics, doped 6h-BaTiO₃ ceramics require a high sintering temperature of greater than 1300 °C, which restricts the possibility of cofiring with other components. Up to now, no report has been found in the literature regarding the low sintering temperature of hexagonal BaTiO₃ ceramics. It is thus our motivation to reduce the sintering temperature of Mn-doped 6h-BaTiO₃ below 1000 °C while retaining the hexagonal structure and microwave dielectric properties.

In the present study, Ba(Ti_{1-x}Mn_x)O₃ with $x=0.15$ [Ba(Ti_{0.85}Mn_{0.15})O₃] was used as host material since the pure form of hexagonal phase can be obtained at a calcination temperature of 1100 °C. The host material was then mixed with small amounts of common sintering aids, including Bi₂O₃, B₂O₃, BaSiO₃, Li₂CO₃, CuO, V₂O₅, 5ZnO·2B₂O₃, and 5ZnO·2SiO₂ [10–16], and followed by sintering at different temperatures. The effects of sintering aids on the densification, microstructural evolution, and microwave properties of the 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics were examined and discussed.

2. Experimental procedure

Ba(Ti_{0.85}Mn_{0.15})O₃ powders were prepared by a solid-state reaction technique. High-purity (>99.9% purity) TiO₂, BaCO₃, and MnCO₃ (Merck, reagent grade) were used as raw materials. Oxides based on the compositions of Ba(Ti_{0.85}Mn_{0.15})O₃ were mixed and milled in methyl alcohol solution using polyethylene jars and zirconia balls for 24 h, and then dried at 80 °C in an oven overnight. After drying, the powders were calcined at 1100 °C for 4 h. Phase identification on the calcined powders was performed using X-ray diffraction (XRD, Rigaku DMX-2200). The calcined Ba(Ti_{0.85}Mn_{0.15})O₃ powder was mixed with different amounts of sintering aids

* Corresponding author. Present Address: National Taipei University of Technology, Department of Materials and Mineral Resources Engineering, 1, Sec. 3, Chung-Hsiao E. Road, Taipei 106, Taiwan, ROC. Tel.: +886 2 2771 2171x2735; fax: +886 2 27317185.

E-mail address: seafuewang@yahoo.com (S.-F. Wang).

(Bi_2O_3 , B_2O_3 , BaSiO_3 , Li_2CO_3 , $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$, $5\text{ZnO}\cdot 2\text{SiO}_2$) and remilled in methyl alcohol for 24 h. The powders after drying were determined to have a particle size of $\approx 0.7\ \mu\text{m}$ by light scattering (Horiba, LA-950). The powders were added with 5 wt% of a 15% PVA solution and pressed into disc-shaped compacts at a uniaxial pressure of 120 MPa. The obtained samples were then heat-treated at $550\ ^\circ\text{C}$ for 2 h to eliminate PVA, followed by sintering in the temperatures ranging from 800 to $1200\ ^\circ\text{C}$ for 2 h at a heating rate of $10\ ^\circ\text{C}/\text{min}$.

The densities of the samples were measured by a liquid displacement method. X-ray diffraction (Rigaku DMX-2200) with monochromatic $\text{Cu-K}\alpha$ radiation was performed for the phase identification of the ground-sintered ceramic powders. Scanning electron microscopy (SEM; Hitachi S4700) and energy-dispersive spectroscopy (EDS) were performed on the sintered surfaces to characterize microstructures. The dielectric constants (ϵ_r) and unloaded Q values at microwave frequencies were measured in the TE_{018} mode by a Hakki and Coleman method [17]

with a network analyzer (HP 8722ES). The temperature coefficient of the resonance frequency (τ_f) was measured in a low-temperature Delta Design box furnace in the temperature range from 25 to $85\ ^\circ\text{C}$.

3. Results and discussion

The host material of $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ powders, prepared from solid-state reaction at $1100\ ^\circ\text{C}$, consists of hexagonal (6h) BaTiO_3 structure [space group of $P6_3/mmc$ (No. 194), and lattice parameters of $a = 0.572\ \text{nm}$ and $c = 1.396\ \text{nm}$ (JCPDS 34-0129)], though a very trace amount of 12R polytype [similar to trigonal- BaFeO_3 structure (JCPDS 74-0646, No. 166, $R\bar{3}m$, $a = 0.569\ \text{nm}$, $c = 2.801\ \text{nm}$)] was

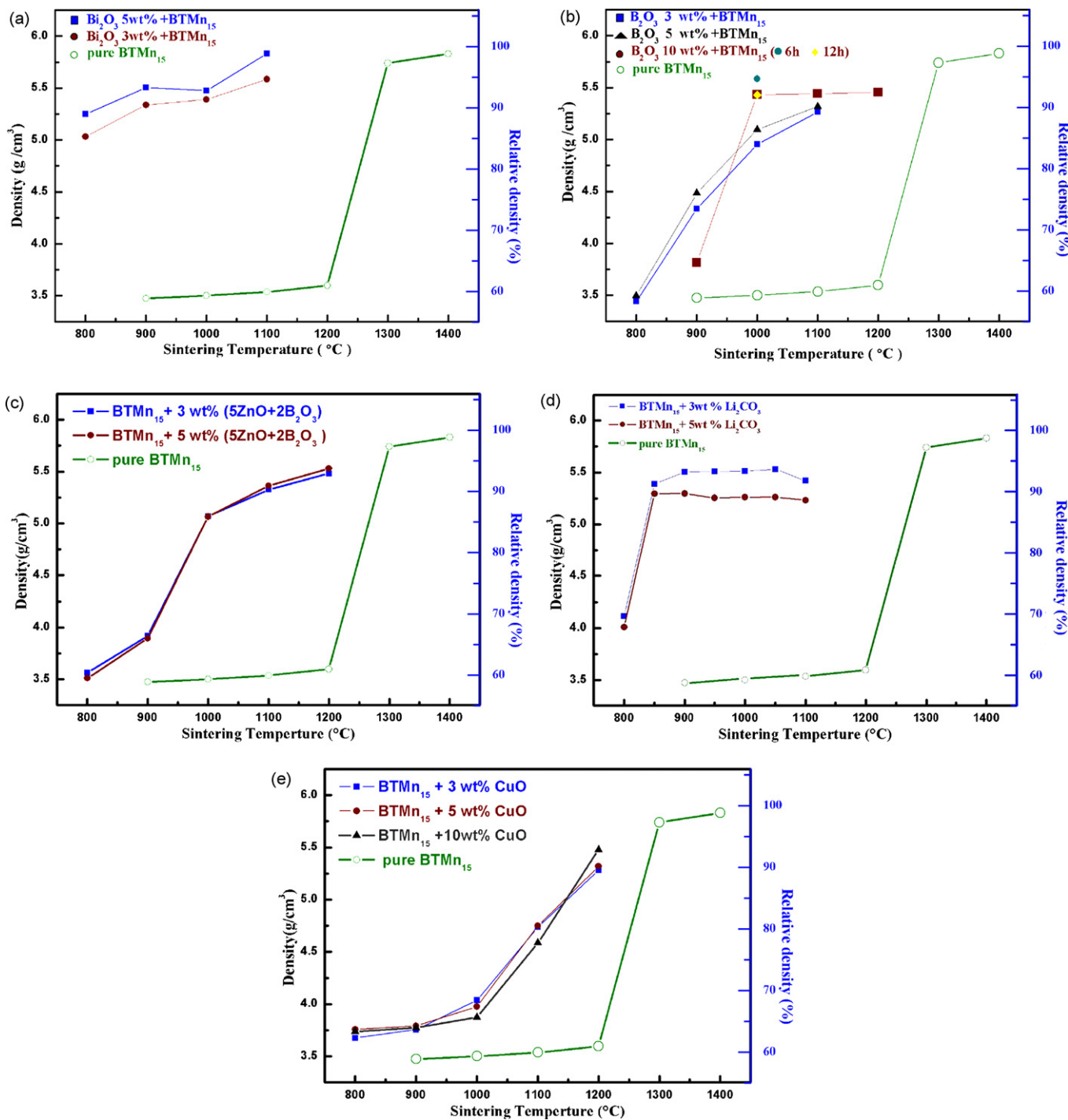


Fig. 1. Sintered densities of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of (a) Bi_2O_3 , (b) B_2O_3 , (c) $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$, (d) Li_2CO_3 , and (e) CuO , sintered at various temperatures.

also observed [18]. When the host material was sintered, hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with density of 5.72 g/cm^3 (97.6% of theoretical density) can be achieved at the sintering temperature of $\approx 1300^\circ\text{C}$, which is similar to that of common tetragonal BaTiO_3 ceramics. Average grain size of $\approx 2.1 \mu\text{m}$, evaluated based on the SEM micrographs by a linear intercept method [19], was obtained. The ε_r , Q_f , and τ_f values of the host material sintered at 1300°C are 61.1, 10,010, and $207.0 \text{ ppm}/^\circ\text{C}$, respectively.

In order to lower the sintering temperature of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$, several fluxes including Bi_2O_3 , B_2O_3 , BaSiO_3 , Li_2CO_3 , CuO , V_2O_5 , $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$, and $5\text{ZnO}\cdot 2\text{SiO}_2$, commonly used in tetragonal BaTiO_3 were selected in this study. The sintered densities of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of various fluxes sintered at different temperatures are shown in Fig. 1. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with most of the flux additions can be efficiently densified at temperatures less than 1200°C , except those ceramics with the additions of $5\text{ZnO}\cdot 2\text{SiO}_2$, BaSiO_3 , and V_2O_5 , which indicate a negligible densification and therefore were not further examined. XRD patterns and surface SEM micrographs on the selected densified $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of various fluxes are shown in Figs. 2 and 3, respectively. Microwave dielectric properties of ε_r and Q_f values for hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of various fluxes sintered at different temperatures are shown in Fig. 4 and a selected list of the results are indicated in Table 1.

3.1. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ with addition of Bi_2O_3

Results shown in Fig. 1(a) indicate that an addition of 5 wt% Bi_2O_3 significantly increases the density of $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic at the sintering temperature as low as 900°C , which is almost 400°C lower than that of the pure $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic. A pure 6h- $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with a little amount of Bi_2O_3 phase was obtained with the disappearance of the 12R- BaFeO_3 polytype structure, as shown in Fig. 2(a). Density of 5.83 g/cm^3 (99.5% theoretical) can be achieved at sintering temperature of 1100°C . It appears that the grain growth was inhibited by the addition of Bi_2O_3 during sintering. An average grain size of $\approx 0.8 \mu\text{m}$ was observed at the sintering temperature of 900°C for host material with 5 wt% Bi_2O_3 . Carefully examining the SEM micrograph, a second phase was observed at the grain boundaries. The effect of Bi_2O_3 addition on the microstructural evolution of hexagonal BaTiO_3 is similar to that observed in the tetragonal BaTiO_3 , reported by Kumar et al. [14].

Fig. 4(a) shows the microwave dielectric properties of the 6h- $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of 3 and 5 wt% Bi_2O_3 . Both the dielectric constant and the quality factor are diluted by the addition of Bi_2O_3 , but change in the temperature coefficient of the

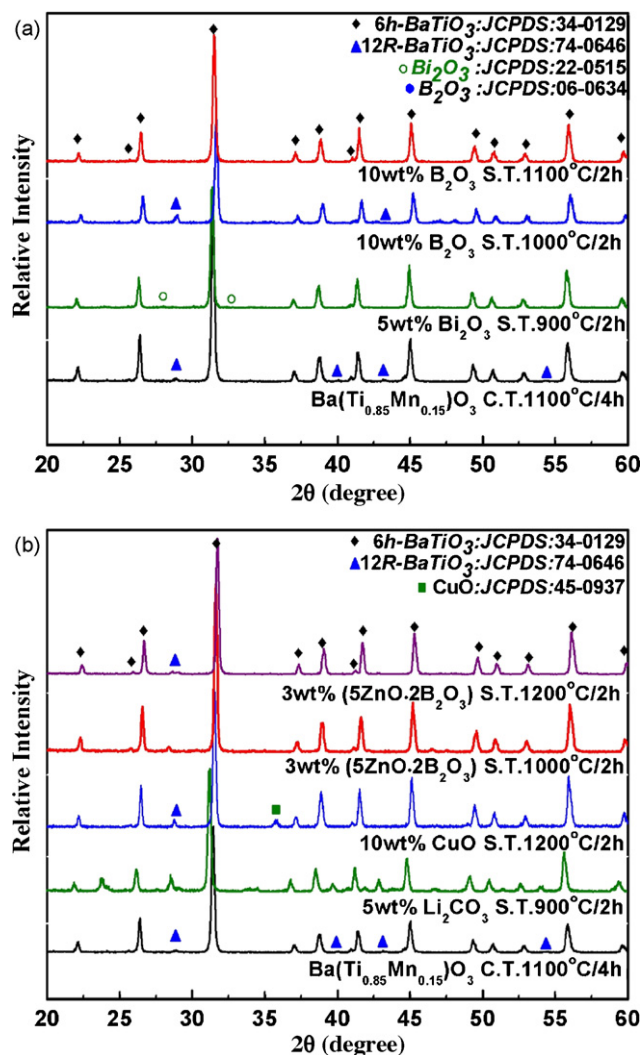


Fig. 2. XRD patterns of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of (a) 5 wt% Bi_2O_3 sintered at 900°C and 10 wt% B_2O_3 sintered at 1000°C , 1100°C , and (b) 3 wt% $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$ sintered at 1000°C , 1200°C , 5 wt% Li_2CO_3 sintered at 900°C , and 10 wt% CuO sintered at 1200°C .

resonance frequency is trivial. Dielectric constant increases with the sintering temperature and the amount of Bi_2O_3 , and is in turn strongly correlated to the trends of sintering densities. Generally the Q_f value decreases with the sintering temperature, which is due to the interaction of Bi_2O_3 and host material at high temperatures

Table 1

A selected list of microwave dielectric properties for fluxed and sintered hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics.

Sintering aid (wt%)	Sintering temperature ($^\circ\text{C}$)	Sintered density (g/cm^3)	Microwave properties			
			f (GHz)	ε_r	Q_f (GHz)	τ_f ($\text{ppm}/^\circ\text{C}$)
–	1300	5.70	–	61.1	10010	207.0
3 wt% Bi_2O_3	900	5.34	7.2	50.3	1241	119.7
5 wt% Bi_2O_3	900	5.51	8.1	54.7	1323	183.3
10 wt% Bi_2O_3	1000	5.43	6.9	52.1	1770	271.7
3 wt% $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$	1100	5.44	6.8	54.4	3448	254.5
3 wt% $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$	1000	5.01	6.5	55.8	1960	197.2
3 wt% Li_2CO_3	1200	5.48	6.7	54.5	4837	183.2
5 wt% Li_2CO_3	850	5.39	6.9	51.4	1391	–
5 wt% Li_2CO_3	950	5.51	7.0	51.5	1352	49.4
10 wt% CuO	850	5.29	7.9	43.0	1536	–
10 wt% CuO	950	5.25	7.9	43.7	2501	–29.8
10 wt% CuO	1200	5.48	7.1	51.0	4586	152.3

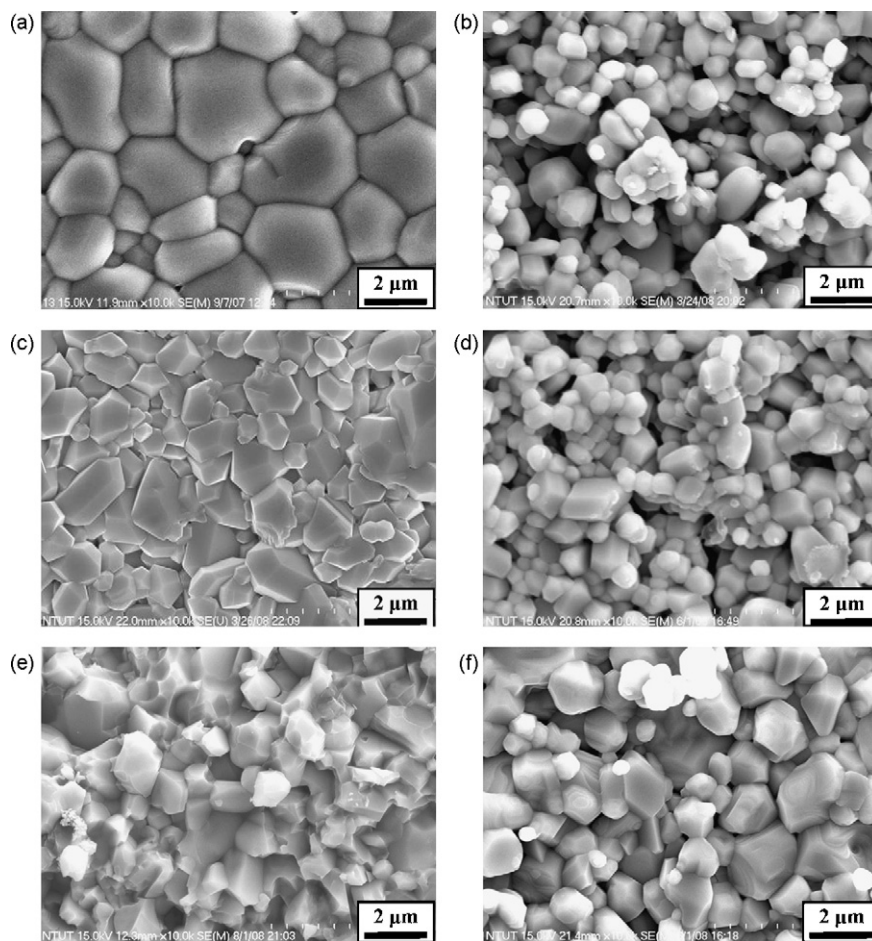


Fig. 3. Surface SEM micrographs of (a) pure hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic sintered at 1300°C , and that with additions of (b) 5 wt% B_2O_3 sintered at 900°C , (c) 10 wt% B_2O_3 sintered at 1000°C , (d) 3 wt% $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$ sintered at 1000°C , (e) 3 wt% Li_2CO_3 sintered at 900°C , and (f) 10 wt% CuO sintered at 1200°C .

that poisons the quality factor. The best results obtained in this study were ε_r of 54.7, Q_f of 1323, and τ_f of $183.4 \text{ ppm}/^\circ\text{C}$.

3.2. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ with addition of B_2O_3

Fig. 1(a) shows the sintered density versus sintering temperature for the host material with various amounts of B_2O_3 . Addition of B_2O_3 significantly reduces the densification temperature of the host material. The sintered densities of the samples increase with the extent of B_2O_3 . In order to reduce the sintering temperature to below 1000°C , 10 wt% of B_2O_3 was added into the post-calcined $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ powders. Density of $5.4 \text{ g}/\text{cm}^3$ for the ceramic was obtained. Increasing the soaking time from 2 to 6 h has an obvious change in the density ($5.58 \text{ g}/\text{cm}^3$). However, further increase in the soaking time results in reduction of sintered density, due to the evaporation of B_2O_3 and the trapped porosity [15]. For the sintering temperatures below 1100°C , a minor phase of 12R polytype structure and a second phase of B_2O_3 were present in the ceramics [Fig. 2(a)]. Very dense microstructure with an average grain size of $1.9 \mu\text{m}$ for host material with 10 wt% B_2O_3 sintered at 1000°C for 6 h was seen, as shown in Fig. 3(c).

The microwave dielectric properties of the host materials with 10 wt% B_2O_3 addition and sintered at various temperatures are shown in Fig. 4(c). The ε_r , Q_f , and τ_f values for the ceramics sintered at 1000 and 1100°C are 52.1, 1770, and $271.7 \text{ ppm}/^\circ\text{C}$, and 54.4, 3448, and $254.5 \text{ ppm}/^\circ\text{C}$, respectively. Increasing the soaking time at 1000°C does not further improve the microwave dielectric properties of the ceramics.

3.3. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ with addition of Li_2CO_3

Among the fluxes studied, Li_2CO_3 is the most effective sintering aid for the hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic, similar to that observed in tetragonal BaTiO_3 [20–22]. Maximum sintered densities were achieved at the sintering temperatures of 900 and 850°C for the addition of 3 and 5 wt% Li_2CO_3 , respectively. Above the temperature at which maximum density was achieved, the sintered density levels off. The sintered density decreases with increasing the Li_2CO_3 content due to the light weight nature of Li compounds. Only 6h- and 12R- $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ phases are present in the XRD patterns and no detectable second phase was observed, as shown in Fig. 2(b). Grain size of the $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics sintered with Li_2CO_3 increases significantly with sintering temperature and the content of the Li_2CO_3 , which is commonly reported in the liquid phase sintering of ceramics. Fig. 3(c) shows the dense microstructure of the $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 3 wt% of Li_2CO_3 sintered at 900°C , in which the average grain size is $1.6 \mu\text{m}$.

As shown in Fig. 4(c), the change in dielectric constant of the $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with Li_2CO_3 additions is insignificant, while it follows the path of sintered density versus temperature profile very well. The dielectric constants of ceramics with 3 and 5 wt% of Li_2CO_3 and sintered at 850°C are 51.4 and 43, respectively. Clearly, dielectric constants of the ceramics were diluted by the presence of the second phase. It may be attributed to the LiTiO_2 phase, similar to that reported in the study of tetragonal BaTiO_3 with addition of Li compounds by Randall et al. [20] and Lin and Wu [21]. The Q_f values for this system are around 2000, though a

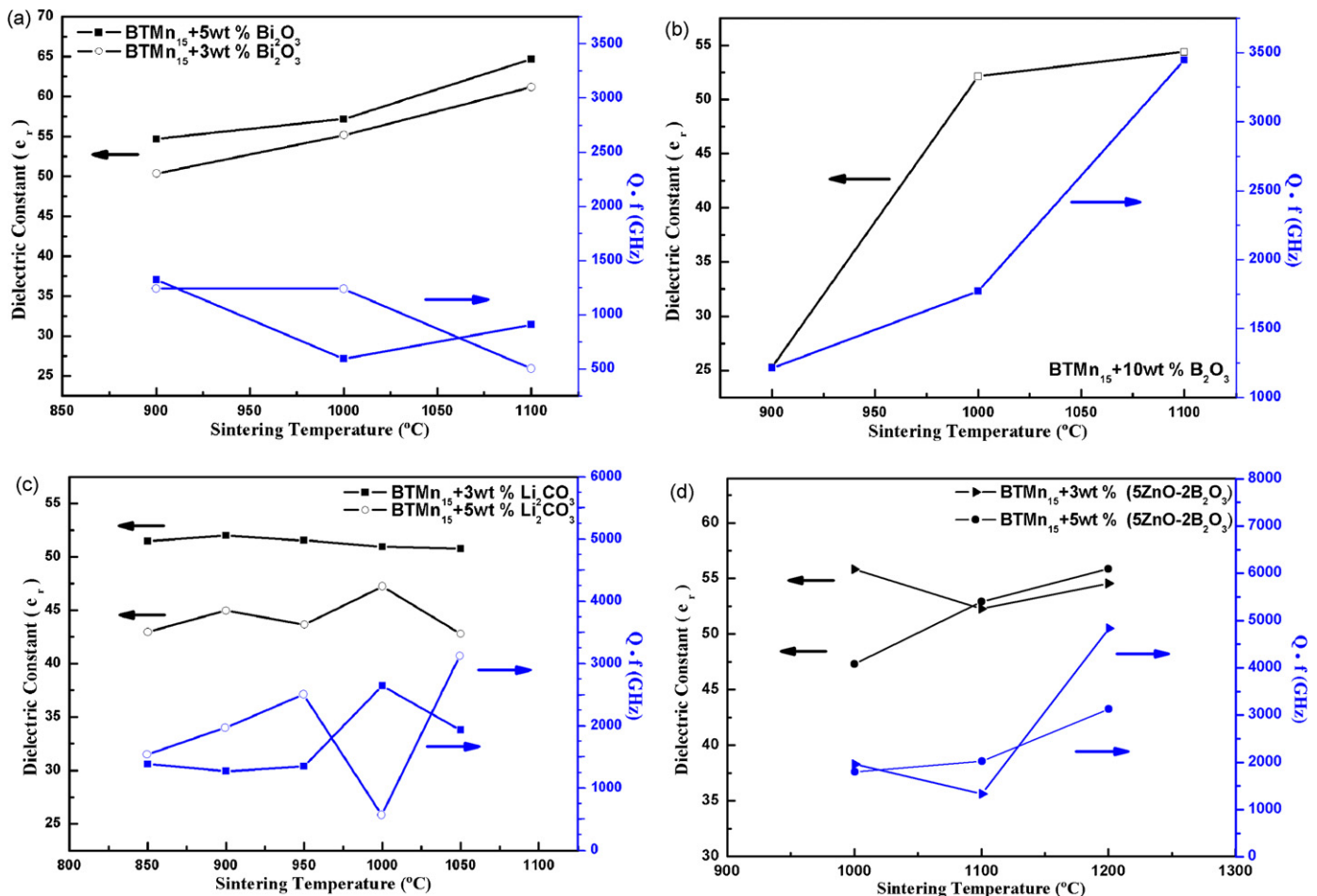


Fig. 4. Microwave dielectric properties of ϵ_r and Q_f values for hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics with additions of (a) Bi_2O_3 , (b) B_2O_3 , (c) $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$, and (d) Li_2CO_3 , sintered at various temperatures.

variation exists. The τ_f values for the ceramics with 3 and 5 wt% of Li_2CO_3 and sintered at 950 $^\circ\text{C}$ are 49.4 and -29.8 ppm/ $^\circ\text{C}$ (Table 1), respectively, which are different from those ceramics with additions of other fluxes that do not affect the τ_f value of the sintered ceramic. The reduction in τ_f value associated with the Li_2CO_3 addition may be due to the incorporation of Li^+ ions into the B-sites of $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ structures, similar to that reported in the low-temperature phases (tetragonal and cubic) of $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_3$ [22].

3.4. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ with addition of $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$

Fig. 1(c) shows the sintered density of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 3 and 5 wt% $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass at different sintering temperatures. It seems that the extent of $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass does not have a strong effect on the densification, as observed in other microwave materials [15,23]. The sintered density increases with increasing sintering temperature, in which the density of 5.54 g/cm 3 was obtained at the sintering temperature of 1200 $^\circ\text{C}$. XRD patterns in Fig. 2(b) show the presence of 6h- $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ phase with trace amount of 12R polytype. No other phase is visible in XRD patterns. Microstructure with an average grain size of 0.8 μm and a wide grain size distribution was obtained for the 6h- $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 3 wt% $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass sintered at 1000 $^\circ\text{C}$. Fig. 4(d) shows the ϵ_r and Q_f values of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 3 and 5 wt% $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass at different sintering temperatures. Best results are obtained in the sample containing 3 wt% $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass and sintered at 1200 $^\circ\text{C}$, in which the ϵ_r , Q_f , and τ_f values are 54.5, 4837,

and 183.2 ppm/ $^\circ\text{C}$, respectively, as listed in Table 1. The microwave dielectric properties are closely correlated to the density of the $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic. The small effect of $5\text{ZnO} \cdot 2\text{B}_2\text{O}_3$ glass on the densification behavior and microwave dielectric properties of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic implies only little chemical interaction between the glass and the host material.

3.5. Hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ with addition of CuO

CuO is a common sintering aid for microwave materials, which has a melting point of 1446 $^\circ\text{C}$. Liquid phase was generated at high temperatures due to the interaction between CuO and Cu_2O . Densification of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 3, 5, and 10 wt% CuO at different sintering temperatures is shown in Fig. 1(e). The sintered density increases with increasing sintering temperature, but the extent of CuO does not seem to affect the densification. The results indicated that density of 5.3 g/cm 3 (about 93% theoretical density of pure BaTiO_3) was achieved at sintering temperature of 1200 $^\circ\text{C}$. The effect of the CuO addition on the densification of hexagonal $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramics is limited. XRD results [Fig. 2(b)] indicate a major hexagonal phase, a minor phase of 12R polytype structure, and a trace amount of CuO phase in the ceramics. BaCuO_2 , a second phase observed in the literature [16], was not found in this study. Fig. 3(f) shows the microstructure of the $\text{Ba}(\text{Ti}_{0.85}\text{Mn}_{0.15})\text{O}_3$ ceramic with 10 wt% CuO and sintered at 1200 $^\circ\text{C}$, which has an average grain size of 1.0 μm , and its dielectric properties are listed in Table 1. The ϵ_r , Q_f , and τ_f values for the ceramics are 51.0, 4586, and 152.3 ppm/ $^\circ\text{C}$, respectively. Similar to

5ZnO·2B₂O₃ glass addition, the microwave dielectric properties are closely correlated to density of the Ba(Ti_{0.85}Mn_{0.15})O₃ ceramic.

From the results discussed above, most fluxes used as sintering aids in tetragonal phase of BaTiO₃ also effectively reduce the sintering temperature of hexagonal Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics through liquid phase sintering, without losing the microwave dielectric properties, particularly for the specimens with Bi₂O₃ or Li₂CO₃ additions. The effectiveness of the flux is closely related to the wettability of liquid on the host material and the volume fraction of the liquid phase during sintering [24], which is in turn determined on the level of chemical interaction between the flux and the host material. Similar to other microwave dielectric ceramics, such as Ba₂Ti₂O₉, Ba(Mg_{1/3}Ta_{2/3})O₃, etc., sintered with fluxes, the ϵ_r values are diluted by the presence of the second phase at the grain boundaries, and the Q_f values are degraded by the chemical interaction of the host materials and the fluxes, which reduces the ordering of the structure or decreases the chemical purity. The τ_f values of the fluxed and sintered ceramics are dependent on the substitutions of the foreign ions which alters the tilt angle of the TiO₆-octahedron.

4. Conclusion

In this study, 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ with additions of various sintering aids, including Bi₂O₃, B₂O₃, BaSiO₃, Li₂CO₃, CuO, V₂O₅, 5ZnO·2B₂O₃, and 5ZnO·2SiO₂, were sintered at different temperatures. The effects of sintering aids on the densification, microstructural evolution, and microwave properties of the 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics were examined. Among the fluxes studied, Bi₂O₃, B₂O₃, and Li₂CO₃ were found to be effective sintering aids for the 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics. Results indicate that the best results were obtained for the compositions of 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ with the additions of 5 wt% Bi₂O₃ sintered at 900 °C (ϵ_r : 54.7, Q_f : 1323, and τ_f : 183.3 ppm/°C), 10 wt% B₂O₃ sintered at 1100 °C (ϵ_r : 54.4, Q_f : 3448, and τ_f : 254.5 ppm/°C), and 5 wt% Li₂CO₃ sintered at 950 °C (ϵ_r : 43.7, Q_f : 2501, and τ_f :

–29.8 ppm/°C). These results suggest that 6h-Ba(Ti_{0.85}Mn_{0.15})O₃ ceramics can be sintered with fluxes at temperatures lower than 1100 °C through liquid phase sintering, while retaining its hexagonal structure and microwave dielectric properties.

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