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Densification, microstructural evolution and microwave dielectric properties of fluxed sintered 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics

Sea-Fue Wang *, Yung-Fu Hsu, Hsin-Sian Huang, Yu-Jung Liu

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

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Abstract

Doped hexagonal $BaTiO_3$ (h-$BaTiO_3$) ceramics have recently been identified as potential candidates for use in microwave dielectric resonators. However, similar to other common microwave ceramics, doped h-$BaTiO_3$ ceramics require a sintering temperature higher than 1400 °C. In this study, the effects of Bi_2O_3 and Li_2CO_3 on the densification, microstructural evolution and microwave properties of hexagonal 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics were examined. Results indicate that Bi_2O_3 and Li_2CO_3 are able to effectively reduce the sintering temperature of 12R-$Ba(Ti_{05}Mn_{0.5})O_3$ ceramics through liquid phase sintering while retaining the hexagonal structure and the microwave dielectric properties. The best results were obtained for the 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ with the additions of 5 wt% Bi_2O_3 sintered at 1200 °C (ε_r: 36.0, Qf_r: 6779 GHz, and τ_f: 25.3 ppm/°C), and 5 wt% Li_2CO_3 sintered at 1200 °C (ε_r: 28.1, Qf_r: 5304 GHz, and τ_f: 35.3 ppm/°C).

Keywords: Microwave properties; h-$BaTiO_3$; Liquid phase sintering; Microstructure

1. Introduction

Commercial wireless communication has been a rapid growth market during the past decade. Technological advancements in this field have been made possible, in part, by the recent revolution in the miniaturization of microwave circuits due to the introduction of high dielectric constant (ε_r), low-loss (high Q), and temperature stable (low τ_f) dielectric resonators. Several ceramic materials, including $(Zr_{0.8}Sn_{0.2})TiO_4$, Ba(Zn,-Ta)O_3, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and $BaO–R_2O_3–TiO_2$ (R = rare earth ions) systems, have been developed for use in microwave resonators [1–4].

Investigating the microwave properties of doped h-$BaTiO_3$ ceramics in their recent studies, Wang et al. and Sinclair et al. [5–8] found the materials a promising candidate for use in ceramic resonators. However, similar to common microwave ceramics, doped h-$BaTiO_3$ ceramics require a high sintering temperature exceeding 1400 °C, a restriction against the possibility of cofiring with other components. A previous report [9] suggested that Bi_2O_3, B_2O_3, and Li_2CO_3 could effectively reduce the sintering temperature of h-$Ba(Ti_{0.85}Mn_{0.15})O_3$ ceramics through liquid phase sintering without compromising the hexagonal structure. However, the fluxed sintered h-$Ba(Ti_{0.85}Mn_{0.15})O_3$ ended up with inferior microwave dielectric properties.

In the study, instead of $Ba(Ti_{0.85}Mn_{0.15})O_3$, $Ba(Ti_{0.5}Mn_{0.5})O_3$ with a τ_f value close to zero was used as the host material to improve microwave dielectric performance. The host material was first mixed with small amounts of common sintering aids, including Bi_2O_3 and Li_2CO_3, followed by sintering at different temperatures. The effects of these sintering aids on the densification, microstructural evolution and microwave properties of the h-$Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics were examined and discussed.

1.1. Experimental procedure

$Ba(Ti_{0.5}Mn_{0.5})O_3$ powders were prepared by a solid-state reaction technique. High-purity (>99.9% purity) TiO_2, $BaCO_3$, and $MnCO_3$ (Merck, reagent grade) were used as raw materials. Oxides based on the compositions of $Ba(Ti_{0.5}Mn_{0.5})O_3$ were mixed and milled in methyl alcohol solution using polyethylene

* Corresponding author. Present address: Dept. of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan, ROC. Tel.: +886 2 2771 2171x2735.
E-mail address: seafuewang@yahoo.com (S.-F. Wang).

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jars and zirconia balls for 24 h, and then dried at 80 °C in an oven overnight. After drying, the powders were calcined at 1150 °C for 4 h. Phase identification on the calcined powders was performed using X-ray diffraction (XRD, Rigaku DMX-2200). The calcined $Ba(Ti_{0.5}Mn_{0.5})O_3$ powders were mixed with different amounts of sintering aids (Bi_2O_3, Li_2CO_3) and remilled in methyl alcohol for 24 h. The powders were then added with 5 wt% of a 15 wt% PVA solution and pressed into disc-shaped compacts at a uniaxial pressure of 120 MPa. The obtained samples were heat-treated at 550 °C for 2 h to eliminate PVA, followed by sintering at the temperatures ranging from 900 to 1300 °C for 2 h at a heating rate of 10 °C/min. In order to understand the effects of fluxes on the sintering characteristic, dilatometric analyses were performed to characterize the shrinkage of the ceramics with respect to temperature. Experiments were conducted using a dilatometer (NETZSCH DIL 402C) in air and at a heating rate of 10 °C/min. This method makes it possible to trace the onset temperature of the densification during sintering.

The densities of the samples were measured by a liquid displacement method. XRD with monochromatic Cu-Kα radiation was performed for 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 $TE_{01\delta}$ mode by the Hakki and Coleman method [10] 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 at the temperatures ranging from 25 to 85 °C.

2. Results and discussion

The host material of $Ba(Ti_{0.5}Mn_{0.5})O_3$ powders, prepared from solid state reaction at 1150 °C, demonstrated a hexagonal (12R) $BaTiO_3$ structure [space group of *R3m* (No.166), and lattice parameters of $a = 0.569$ nm and $c = 2.801$ nm (JCPDS 74-0646)], though a trace amount of 6 h polytype (JCPDS 34-0129, No. 194, $P6_3/mmc$, $a = 0.572$ nm, $c = 1.396$ nm] was also observed [11]. When the host material was sintered, a hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic with a density of 5.70 g/cm^3 (93.3% of theoretical density) could be achieved at the sintering temperature of ≈1450 °C [8,9]. The ε_r, Qf and τ_f values of the host material sintered at 1450 °C read respectively 32.8, 6453 GHz, and 9.6 ppm/°C.

To lower the sintering temperature of the hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$, Bi_2O_3 and Li_2CO_3 fluxes were selected in this study. The sintered densities of the fluxed hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics sintered at different temperatures were shown in Fig. 1. The sintering shrinkage of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic with 5 wt% Bi_2O_3 and 5 wt% Li_2CO_3 with respect to temperature are shown in Fig. 2. The XRD patterns and surface SEM micrographs on the selected densified $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics with additions of 5 wt% Bi_2O_3 and 5 wt% Li_2CO_3 were presented respectively in Figs. 3 and 4. Selected results of microwave dielectric properties including ε_r and Qf_r values for the fluxed hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics sintered at different temperatures were listed in Table 1.

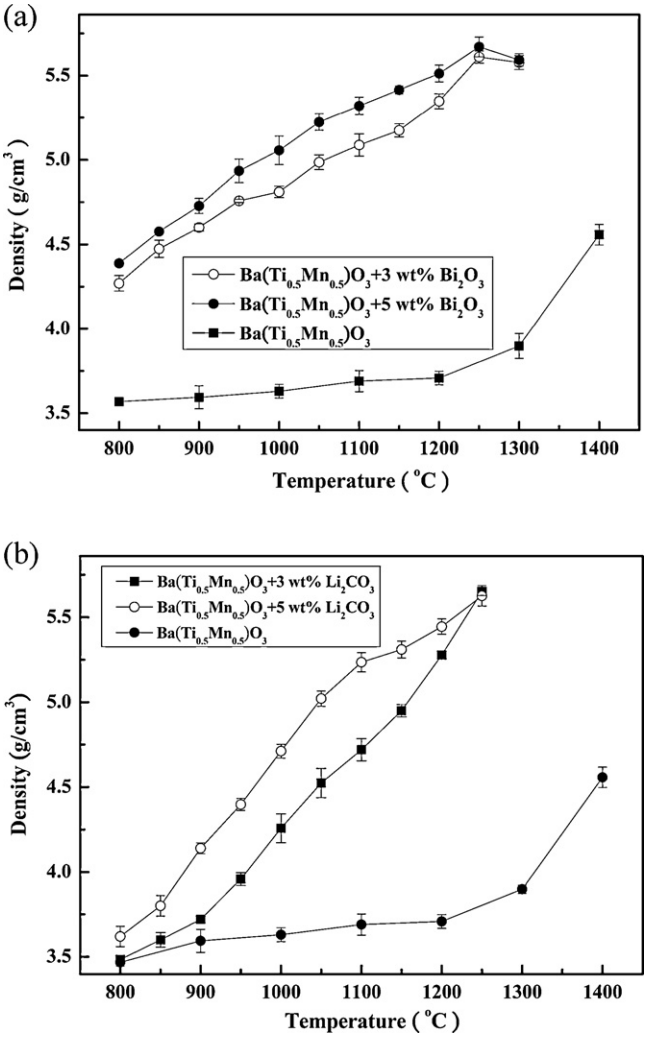

Fig. 1. Sintered densities of hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics with additions of (a) Bi_2O_3 and (b) Li_2CO_3, sintered at various temperatures.

2.1. Hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ with addition of Bi_2O_3

Results shown in Fig. 1(a) indicate that addition of 3 wt% or 5 wt% Bi_2O_3 led to a nearly linear increase in the density of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic at the sintering temperature up to 1250 °C, and the sintered densities reached maxima at 1250 °C, 200 °C lower than that of the pure $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic. Fig. 2(a) compares the dilatometric results of the pure $Ba(Ti_{0.5}Mn_{0.5})O_3$ and its 5 wt% Bi_2O_3-added counterpart. The pure $Ba(Ti_{0.5}Mn_{0.5})O_3$ did not show any visible shrinkage until 1300 °C while the shrinkage of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ added with 5 wt% Bi_2O_3 begun at ≈712 °C, slowly increased with temperature, and showed no sign of leveling off even as the temperature reached 1400 °C. The shrinkage profiles with respect to temperature in Fig. 2(a) are consistent with the profile

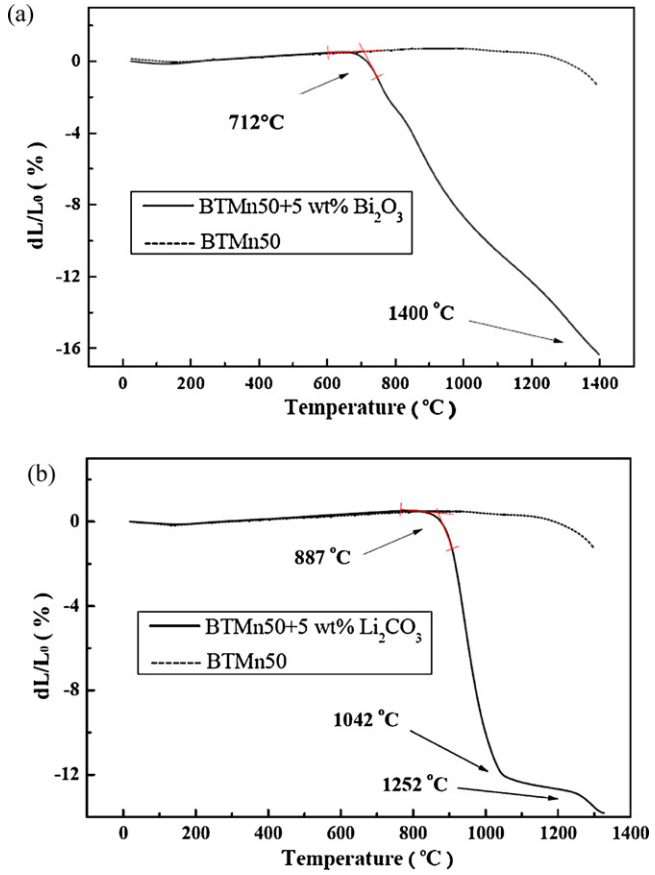

Fig. 2. Sintering shrinkage of hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics with additions of (a) 5 wt% Bi_2O_3 and (b) 5 wt% Li_2CO_3 at temperatures up to 1400 °C.

of sintered density with sintering temperature shown in Fig. 1(a). The continuous heating on the test specimens during dilatometric analysis would defer the temperature at which maximum density was obtained to a higher degree as compared with that of the sintering study (isothermal soaking at each sintering temperature). It is expected that $Ba(Ti_{0.5}Mn_{0.5})O_3$ would densify at a lower temperature (<1250 °C) if more Bi_2O_3 is added to provide more liquid phase during sintering [12]. However, the presence of the second phase at the grain boundaries after sintering would significantly dilute the microwave dielectric properties of the ceramic to a level that it is no longer of use in practical applications.

A hexagonal 12R phase of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic with a little amount of Ba_2TiO_4 phase was obtained for the $Ba(Ti_{0.5}Mn_{0.5})O_3$ sintered with Bi_2O_3, as shown in Fig. 3(a). It is reported that the Mn^{3+} would transfer to Mn^{4+} as the sintering temperature increases, resulting in the formation of a hexagonal 12R phase instead of a 6 h phase [7]. It appeared in the study that the grain growth was inhibited by the addition of Bi_2O_3 during sintering. An average grain size of ≈1–2 μm was observed at the sintering temperature of 1200 °C for the host material with 5 wt% Bi_2O_3 as shown in Fig. 4(a). The effect of Bi_2O_3 addition on the microstructural evolution of the hexagonal $BaTiO_3$ is similar to the one observed in the tetragonal $BaTiO_3$ as reported by Kumar et al. [13].

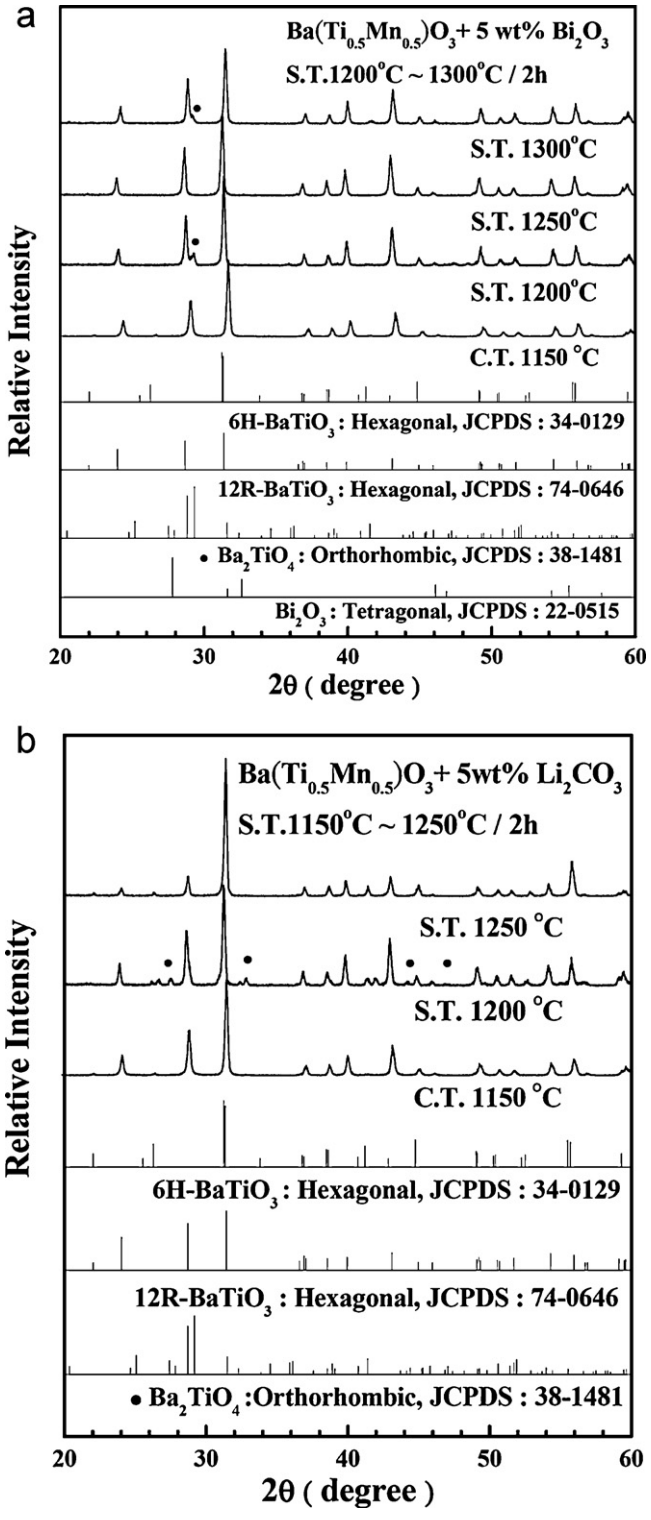

Fig. 3. XRD patterns of hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics with additions of (a) 5 wt% Bi_2O_3 and (b) 5 wt% Li_2CO_3 sintered at various temperatures.

Table 1 shows the microwave dielectric properties of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics with additions of 3 and 5 wt% Bi_2O_3. The dielectric constant was slightly diluted by the addition of Bi_2O_3; however, change in the quality factor was trivial. Dielectric constant was affected by the sintering temperature and the amount of Bi_2O_3. The *Qf* value decreased

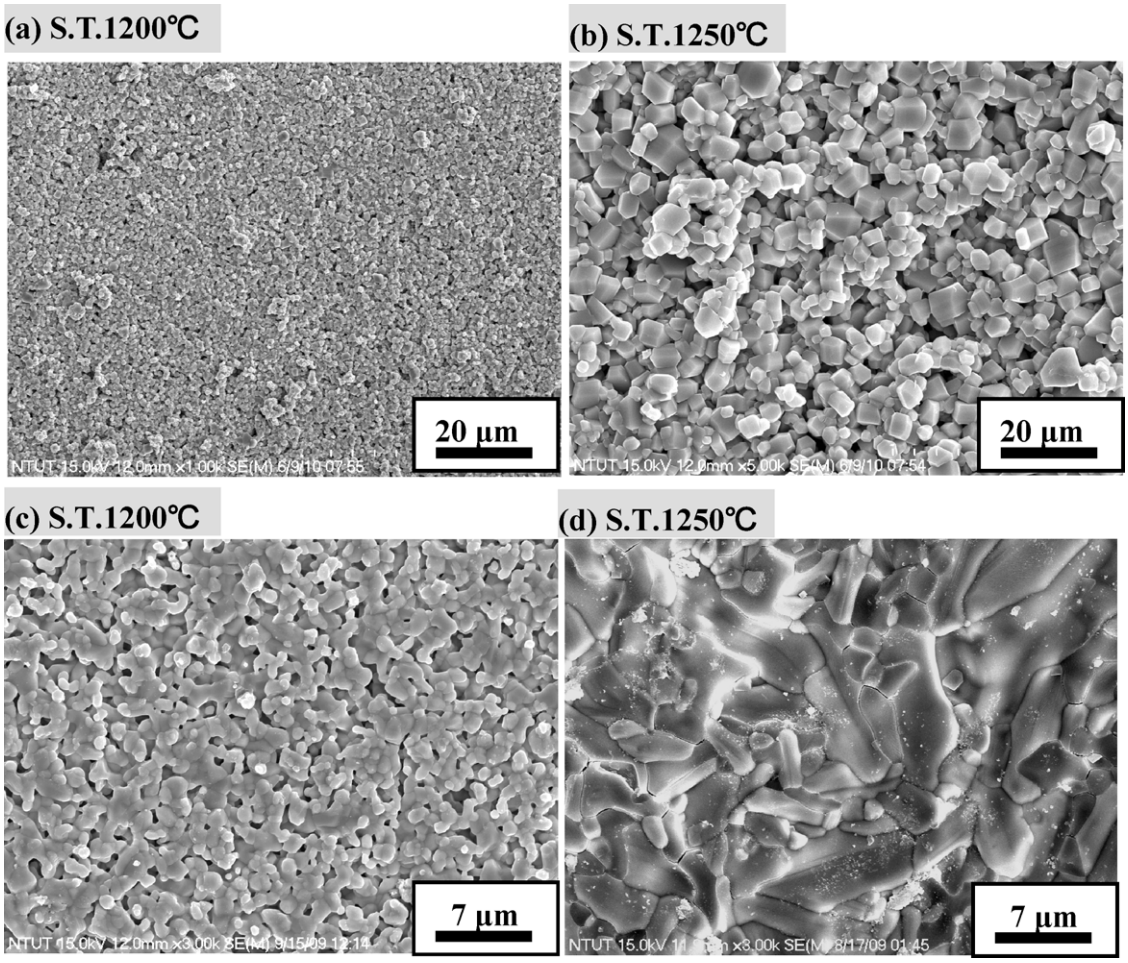

Fig. 4. Surface SEM micrographs of hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ with addition of (a) 5 wt% Bi_2O_3 sintered at 1200 °C, (b) 5 wt% Bi_2O_3 sintered at 1250 °C, (c) 5 wt% Li_2CO_3 sintered at 1200 °C, and (d) 5 wt% Li_2CO_3 sintered at 1250 °C.

with the sintering temperature due to the interaction between Bi_2O_3 and the host material at high temperatures that cripples the quality factor.

2.2. Hexagonal $Ba(Ti_{0.85}Mn_{0.15})O_3$ with addition of Li_2CO_3

Fig. 1(b) shows the sintered density vs. sintering temperature for the host material with 3 at.% and 5 wt% Li_2CO_3. As in the case of $Ba(Ti_{0.5}Mn_{0.5})O_3$ added with Bi_2O_3, addition of Li_2CO_3 reduced the densification temperature of the host material. For the $Ba(Ti_{0.5}Mn_{0.5})O_3$ added with 5 wt% Li_2CO_3 and sintered at 1250 °C, a sintered density of 5.63 g/cm^3 was reached. A major 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ phase with a small amount of h-$Ba(Ti_{0.5}Mn_{0.5})O_3$ and Ba_2TiO_4 phases are present in the XRD patterns, as shown in Fig. 3(b). Grain size of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics sintered with Li_2CO_3 increased significantly with the sintering temperature and the content of

Table 1
A list of selected microwave dielectric properties for fluxed and sintered hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics.

Sintering aid (wt%)	Sintering temperature (°C)	Sintered density (g/cm^3)	Microwave properties			
			f (GHz)	ε_r	Qf (GHz)	τ_f (ppm/°C)
	1550	4.56	10.1	38.4	5444	220.0
3 wt% Bi_2O_3	1200	5.35	9.3	32.8	5191	−17.5
	1250	5.61	9.1	35.0	4501	−87.3
5 wt% Bi_2O_3	1200	5.51	9.2	36.0	6779	25.3
	1250	5.67	10.2	30.1	4340	−2.4
3 wt% Li_2CO_3	1200	5.28	9.3	32.8	5192	−89.9
	1250	5.63	8.8	35.2	1095	−96.0
5 wt% Li_2CO_3	1200	5.45	10.5	28.1	5304	35.3
	1250	5.65	10.5	28.1	1529	29.6

the Li_2CO_3, a common occurrence reported in the liquid phase sintering of ceramics [14]. Fig. 4(c) and (b) show the dense microstructure of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramic with 5 wt% of Li_2CO_3 sintered at 1200 °C and 1250 °C, respectively. Granular grains with sizes around 1–2 μm were observed for the ceramic sintered at 1200 °C. As the sintering temperature increased to 1250 °C, significant grain growth took place and resulted in plate-like grains in the range of 5–20 μm. Careful examination of the SEM micrograph helped identify a second phase at the grain boundaries.

As indicated in Table 1, the dielectric constant of the $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics decreased with Li_2CO_3 additions. The dielectric constants of the ceramics with 3 and 5 wt% of Li_2CO_3 and sintered at 1200 °C read respectively 32.8 and 28.1, showing an obvious dilution by the presence of the second phase, although the sintered density of the former is slightly lowered than that of the latter. This may be attributed to the $LiTiO_2$ phase, similar to the one reported in the studies by Randall et al. [15] and Lin et al. [14] that examined the tetragonal $BaTiO_3$ with addition of Li-compounds. The *Qf* value of the host material with 5 wt% Li_2CO_3 addition was observed to decline rapidly from 5304 GHz at the sintering temperature of 1200 °C to 1529 GHz at 1250 °C. Similar behavior was observed in the host materials with 3 wt% Li_2CO_3. τ_f value of the sintered ceramic with 3 wt% and 5 wt% Li_2CO_3 were around −90 and 30 ppm/°C, respectively. The decrease 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 $Ba(Ti_{0.5}Mn_{0.5})O_3$ structures, similar to the case reported in the low-temperature phases (tetragonal and cubic) of $Ba(Ti_{1-x}, Li_x)O_3$ [16].

As indicated by the results discussed above, Bi_2O_3 or Li_2CO_3 addition helps reduce the sintering temperature of $Ba(Ti_{0.5}Mn_{0.5})O_3$ to a level of 1200 °C through liquid phase sintering. However, it seems impossible to lower the densification temperature to less than 1200 °C without increasing the amount of the added fluxes. The effect of Bi_2O_3 or Li_2CO_3 addition on $Ba(Ti_{0.5}Mn_{0.5})O_3$ appears to be less efficient than the effect on $Ba(Ti_{0.85}Mn_{0.15})O_3$, mainly because that the former consists of much more manganese content which usually inhibits the sintering of $BaTiO_3$. When sintered with Bi_2O_3 or Li_2CO_3 addition, the hexagonal $Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics suffered no significant lose in their microwave dielectric properties. As listed in Table 1, the best results were obtained for the sample containing 5 wt% Bi_2O_3 and 5 wt% Li_2CO_3 additions and sintered at 1200 °C, in which the ε_r, *Qf* and τ_f values read 36.0, 6779 GHz, and 25.3 ppm/°C, and 28.1, 5304 GHz, and 35.3 ppm/°C, respectively.

3. Conclusion

In this study, hexagonal 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ with additions of sintering aids, including Bi_2O_3 and Li_2CO_3, were sintered at different temperatures. The effects of sintering aids on the densification, microstructural evolution and microwave properties of the 12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics were examined. The study indicates that the best results were obtained for the compositions of 12R-$Ba(Ti_{0.85}Mn_{0.15})O_3$ with the additions of 5 wt% Bi_2O_3 sintered at 1200 °C (ε_r: 36.0, Qf_r: 6779 GHz, and τ_f: 25.3 ppm/°C) and 5 wt% Li_2CO_3 sintered at 1200 °C (ε_r: 28.1, Qf_r: 5304 GHz, and τ_f: 35.3 ppm/°C). These results suggest that the hexagonal12R-$Ba(Ti_{0.5}Mn_{0.5})O_3$ ceramics can be sintered with fluxes at the temperature of 1200 °C through liquid phase sintering while retaining its hexagonal structure and microwave dielectric properties.

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