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The effect of glass additives on the microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics

K.P. Surendran[a], P. Mohanan[b], M.T. Sebastian[a,*]

[a]Ceramic Technology Division, Regional Research Laboratory, Industrial Estate, Papanamcode, Trivandrum, Kerala 695 019, India
[b]Department of Electronics, Cochin University of Science and Technology, Cochin 682 022, India

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Abstract

The effect of glass additives on the densification, phase evolution, microstructure and microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) was investigated. Different weight percentages of quenched glass such as B_2O_3, SiO_2, B_2O_3–SiO_2, ZnO–B_2O_3, 5ZnO–$2B_2O_3$, Al_2O_3–SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$, BaO–B_2O_3–SiO_2, MgO–B_2O_3–SiO_2, PbO–B_2O_3–SiO_2, ZnO–B_2O_3–SiO_2 and 2MgO–Al_2O_3–$5SiO_2$ were added to calcined BMT precursor. The sintering temperature of the glass-added BMT samples were lowered down to 1300 °C compared to solid-state sintering where the temperature was 1650 °C. The formation of high temperature satellite phases such as $Ba_5Ta_4O_{15}$ and $Ba_7Ta_6O_{22}$ were found to be suppressed by the glass addition. Addition of glass systems such as B_2O_3, ZnO–B_2O_3, 5ZnO–$2B_2O_3$ and ZnO–B_2O_3–SiO_2 improved the densification and microwave dielectric properties. Other glasses were found to react with BMT to form low-Q phases which prevented densification. The microwave dielectric properties of undoped BMT with a densification of 93.1% of the theoretical density were $\varepsilon_r = 24.8$, $\tau_f = 8$ ppm/°C and $Q_u \times f = 80{,}000$ GHz. The BMT doped with 1.0 wt% of B_2O_3 has $Q_u \times f = 124{,}700$ GHz, $\varepsilon_r = 24.2$, and $\tau_f = -1.3$ ppm/°C. The unloaded Q factor of 0.2 wt% ZnO–B_2O_3-doped BMT was 136,500 GHz while that of 1.0 wt% of 5ZnO–$2B_2O_3$ added ceramic was $Q_u \times f = 141{,}800$ GHz. The best microwave quality factor was observed for ZnO–B_2O_3–SiO_2 (ZBS) glass-added ceramics which can act as a perfect liquid-phase medium for the sintering of BMT. The microwave dielectric properties of 0.2 wt% ZBS-added BMT dielectric was $Q_u \times f = 152{,}800$ GHz, $\varepsilon_r = 25.5$, and $\tau_f = -1.5$ ppm/°C.

Keywords: Dielectric resonator; Microwave dielectric; Complex perovskite; Barium magnesium tantalate; Dielectric properties; Liquid-phase sintering; Glass addition; Cation ordering; Low-loss materials; Low-temperature co-fired ceramics

1. Introduction

In producing miniaturized devices, ceramic multilayer structures with low sintering temperatures are needed because they can be co-fired with low-loss conductors like silver or copper. Low-temperature co-fired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high density, high RF and fast digital applications requiring hermetical packaging and good thermal management [1]. Many new ceramic-glass compositions [2] have recently been developed for microwave applications, especially low permittivity (ε_r) materials using alumina and suitable glass combinations, but also higher dielectric constant materials in the range 20–100 with low dielectric loss. As dielectric resonators, complex perovskite oxides based on $Ba(B'_{1/3}B''_{2/3})O_3$ [B' = Mg, Zn; B'' = Ta, Nb] have shown very interesting properties in the microwave frequency region. In particular, $Ba(Mg_{1/3}Ta_{2/3})O_3$ (abbreviated as BMT) has stimulated a surge of interest for their excellent dielectric properties in the X-band (8–12 GHz) and is considered to be archetypal high Q DR material [3]. The sintering temperature of these ceramics are above 1600 °C which pose practical difficulties for mass production.

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*Corresponding author. Fax: +91-471-249-1712.
E-mail address: mailadils@yahoo.com (M.T. Sebastian).

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A number of strategies have been worked out to reduce the sintering temperature of low-loss materials such as (a) chemical synthesis [4–6], (b) using starting powders with smaller particle size [7] and (c) liquid-phase sintering [8] by adding low melting additive into the ceramic. The chemical synthesis of BMT is not a suitable method for industrial production due to the complexity of the procedures involved, high cost of production and comparatively poor microwave dielectric properties [9]. Chen et al. [10] used NaF as the low melting additives for BMT which suppressed the formation of barium tantalate secondary phases, but the formation of Na_3TaO_4 on the surface has to be controlled to ensure the formation of completely ordered BMT. Boric oxide and copper oxide are the well-known liquid-phase sintering promoters. But there are reports [2] that multi-component glasses are more effective than single-component glass to reduce the sintering temperature of ceramics without considerably damaging the physical properties of the matrix. Recent research trends suggest that glass addition is a useful tool for producing low-loss ceramics like [11,12] $(Zr,Sn)TiO_4$, [13–15] $Ba_2Ti_9O_{20}$, [16–18] $BaTi_4O_9$ and [19–21] $(Mg_{0.5}Ca_{0.5})TiO_3$ at relatively low temperatures of sintering. As an initial study on the interaction of a glass flux with complex perovskite BMT ceramic, Cheng et al. [22,23] observed that adding $MgO–CaO–Al_2O_3–SiO_2$ (MCAS) glass to BMT decreased the sintering temperature down to 1300 °C but the $Q_u \times f$ value has been considerably lowered (9700 GHz) which cannot be afforded in industrial production. In a recent research report Pollet et al. [24] suggested that a combination of B_2O_3 and $LiNbO_3$ can act as a good medium for liquid-phase sintering in BMT but the densification (<95%) and quality factor are not good for applications in multilayer devices. So the search for the right glass composition which aids the vitreous sintering of fully ordered BMT without affecting low-loss quality of the ceramic is a highly challenging problem in microwave ceramics.

After conducting a detailed investigation on the dielectric properties of glasses at ultra-high frequencies, Navias et al. [25] noted that the dielectric losses of borosilicate glasses are comparatively lower than alkali-containing glasses. This is due to the fact that in the latter, alkali ions which are weakly held in the glassy network, absorb energy and eventually give rise to dielectric loss. On the other hand, borosilicate glasses [25,26] have continuous atomic structures, with SiO_4 and BO_3 configurations joined to form (–Si–O–B–O–) linkages, will have high electrical resistance and low dielectric loss. In a recent study [27], the microwave dielectric properties of a few borosilicate glasses ($BaO–B_2O_3–SiO_2$, $PbO–B_2O_3–SiO_2$ and $ZnO–B_2O_3–SiO_2$) have been reported in which it was observed that the τ_f of all these glasses are negative. As cited above, a large number of papers were published on the interaction of glasses with low-loss microwave dielectrics. But the vitreous-phase densification and dielectric loss aspects of silicate/borate and borosilicate glasses in complex perovskites such as BMT which can provide useful information to research on LTCC materials, has not been discussed before. Hence, we have carried out a comprehensive investigation on the liquid-phase sintering effects in BMT using a number of glass systems such as B_2O_3, SiO_2, $B_2O_3–SiO_2$, $ZnO–B_2O_3$, $5ZnO–2B_2O_3$, $Al_2O_3–SiO_2$, $Na_2O–2B_2O_3 \cdot 10H_2O$, $BaO–B_2O_3–SiO_2$, $MgO–B_2O_3–SiO_2$, $PbO–B_2O_3–SiO_2$, $ZnO–B_2O_3–SiO_2$ and $2MgO–2Al_2O_3–5SiO_2$ in an effort to find out an ideal glass system which promotes liquid-phase sintering without deteriorating the microwave dielectric properties. The aims of the research work on BMT with glass addition are (a) to reduce the preparation temperature of BMT and thereby the cost of production without any deterioration in the microwave dielectric properties, (b) to probe the relation between structural order and quality factor, (c) to suppress the formation of secondary phases such as barium tantalates which are detrimental to the microwave quality factor and (d) to improve the microwave dielectric properties of BMT. The influence of the above mentioned glasses on the phase structure, densification, cation ordering and microwave dielectric properties of BMT ceramics are discussed.

2. Experimental

The glass powders used in this investigation were divided into three categories: (i) primary glasses such as B_2O_3 (abbreviated as B), SiO_2 (S), (ii) binary glasses such as $B_2O_3–SiO_2$ (BS), $ZnO–B_2O_3$ (ZB), $5ZnO–2B_2O_3$ (5Z2B), $Al_2O_3–SiO_2$ (AS), $Na_2O–B_2O_3$ (NB), and (iii) ternary glasses such as $BaO–B_2O_3–SiO_2$ (BBS), $MgO–B_2O_3–SiO_2$ (MBS), $PbO–B_2O_3–SiO_2$ (PBS), $ZnO–B_2O_3–SiO_2$ (ZBS) and $2MgO–Al_2O_3–5SiO_2$ (MAL). For synthesizing glasses, high purity (99.9%) oxides/carbonates were weighed stoichiometrically and mixed for 2 h in an agate mortar with pestle using deionized water as the medium. It was then melted in a platinum crucible above their deformation temperature (see Table 1), quenched and powdered. The formation of the glass was confirmed using powder diffraction method. To measure the dielectric properties of the glasses, the powders were added with PVA binder, compacted uniaxially to form thin cylindrical pucks with 14 mm diameter and 1 mm thickness at a pressure of 100 MPa and were sintered at temperatures less than their respective deformation points (see Table 1). The polished thin pellets were electroded by coating silver on both sides in the form of ceramic capacitors and were used for dielectric measurements at low frequencies

Table 1
Physical and electrical properties of glasses

Glass code	Composition (approximate) (mole%)	Density	Softening temp. (°C)	ε_r	Tan δ (at frequency)	Ref.
B	99:B_2O_3	2.46	450	2.47	$5.5\times10-3$ (1 MHz)	[52]
S	99:SiO_2	2.60	1600	3.7	$4.0\times10-4$ (1 MHz)	[31]
BS	40:B_2O_3, 60:SiO_2	2.23	820	4.6	$9.0\times10-4$ (1 MHz)	[52]
ZB	50:ZnO, 50:B_2O_3	3.61	610	6.9	$9.4\times10-3$ (16 GHz)	[27]
5Z2B	71:ZnO, 29:B_2O_3	2.19	567	4.21	$3.3\times10-3$ (1 MHz)	[52]
AS	50:Al_2O_3, 50:SiO_2	2.60	850	8.06	$9.7\times10-3$ (1 MHz)	[52]
NB	8:Na_2O, 15:B_2O_3, 77:H_2O	2.80	75	10.2	$2.1\times10-1$ (1 MHz)	[52]
BBS	30:BaO, 60:B_2O_3, 10:SiO_2	3.40	627	7.2	$4.4\times10-3$ (15 GHz)	[27]
MBS	40:MgO, 40:B_2O_3, 20:SiO_2	3.18	950	5.01	$2.3\times10-3$ (1 MHz)	[52]
PBS	40:PbO, 40:B_2O_3, 20:SiO_2	4.31	448	12.9	$7.1\times10-3$ (12 GHz)	[27]
ZBS	60:ZnO, 30:B_2O_3, 10:SiO_2	3.60	582	7.5	$10.7\times10-3$ (15 GHz)	[27]
MAS	22.2:MgO, 22.2:Al_2O_3, 55.5:SiO_2	2.30	1350	4.5	$7.0\times10-4$ (1 GHz)	[53]

(50 Hz–13 MHz) using an impedance analyzer (HP 4102 A-LF).

High purity (>99.9%) powders of $BaCO_3$ (Aldrich Chemicals), $(MgCO_3)_4Mg(OH)_2.5H_2O$ (Aldrich Chemicals) and Ta_2O_5 (Nuclear Fuel Complex, Hyderabad) were used as the starting materials for the solid-state synthesis of BMT. They were weighed according to the stoichiometric compositions and were ball milled in a plastic bottle using zirconia balls as the milling media in deionized water for 24 h. The slurry was dried in an oven at 100 °C and calcined in platinum crucible at 1200 °C for 10 h with intermediate grinding. The calcined powder was then mixed with different weight percentages of the glass and ground for 2 h and 4 wt% aqueous solution of PVA was added to it as a binder. The powder was uniaxially pressed into cylindrical compacts of 14 mm diameter and 6–8 mm thickness under a pressure of 150 MPa in tungsten carbide dye. The green density of the ceramic pucks were measured using dimensional method. These compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 1 h to expel the binder before they were sintered in the temperature range 1300–1500 °C for 4 h in air at a heating rate of 10 °C/h. The sintered samples were then cooled to 800 °C at a slow rate of 60 °C per hour to enhance cation ordering. The sintering temperature is optimized for each glass ceramic compositions. The polished ceramic pellets with an aspect ratio (diameter-to-height) of 1.8–2.2 which is ideal for maximum separation of the modes, were used for microwave measurements. The bulk density of the sintered samples were measured using Archimedes method. The powdered samples were used for analyzing the X-ray diffraction (XRD) patterns using Cu$K\alpha$ radiation (Philips X-ray Diffractometer). The sintered samples were thermally etched for 30 min at a temperature of about 25 °C below the sintering temperature and the surface morphology was studied using a scanning electron microscope Hitachi SEM Model No. S-4300.

The dielectric properties of the materials were measured in the microwave frequency range using a network analyzer HP 8510C (Hewlett-Packard, Palo Alto, CA). The dielectric constant ε_r was measured by the post-resonator method of Hakki and Coleman [28] and the samples were end shorted with finely polished copper plates coated with gold. The microwave is coupled though E-field probes as described by Courtney [29]. The accuracy of the measurement of dielectric constant is 0.01 and is limited to the accuracy in the measurement of dimension and resonant frequency of the sample. $TE_{01\delta}$ mode of resonance whose Q is intimately related to the dielectric tan δ, is used for the measurements. The unloaded quality factor Q_u of the resonance was determined using a copper cavity whose interior was coated with silver and the ceramic dielectric is placed on a low-loss quartz spacer which reduces effect of losses due to the surface resistivity of the cavity. For measuring Q factor, cavity method is ideal since the electric field is symmetrical with geometry of the cavity and the dielectric [30]. The coefficient of thermal variation of resonant frequency (τ_f) was measured by noting the temperature variation of the resonant frequency of $TE_{01\delta}$ mode in the reflection configuration over a range of temperature 20–80 °C when the sample was kept in the end shorted position.

3. Results and discussion

3.1. Densification

The dielectric properties of most of the ternary glasses we used in this investigation have been reported [26,31] earlier and hence we synthesized those compositions, which exhibited relatively better dielectric properties at microwave frequencies. Very recently, Cheng et al. [32] made a remarkable observation that the reactivity and wettability of sol–gel-derived glasses were inferior to quenched ones. Hence in this investigation, quenched glass compositions were used. Table 1 gives the physical and electrical properties of the glasses used. The major problem with the solid-state sintering of BMT is that the sintering temperature of this ceramic is above 1600 °C and long-time annealing up to several days is needed for achieving an ordered phase of BMT. This can result in two effects: (a) the particle coarsening and consequent generation of porosity occurs when the ceramic is heat treated at high temperatures for long periods of time which is detrimental to the microwave dielectric properties of the sintered ceramic and (b) secondly, the volatilization of the Mg^{2+} ions occurs which results in the formation of low-Q secondary phases such as $BaTa_2O_6$ and $Ba_5Ta_4O_{15}$ which too is undesirable [33]. So for obvious reasons, the low-temperature sintering of low-loss BMT ceramic is of high importance, which can be achieved through vitreous-phase sintering. But, excess addition of glass has been proven to increase the dielectric loss quality of the ceramic, nonetheless a reduction in the sintering temperature.

It has been observed that introducing a glassy material into matrix plays a pivotal role in controlling the phase evolution and densification phenomena in BMT. As a typical case, the behavior of sintered density and microwave quality factors of BMT mixed with 0.5 wt% B_2O_3 as a function of sintering temperature is presented in Fig. 1. The bulk density increased with sintering temperature, reached a maximum (7.47 g/cm^3) at 1340 °C and then decreased with further increase in temperature. At low sintering temperatures, the microwave quality factors were lower due to poor densification and the formation of a number of additional phases. As the sintering temperature rose from 1250 to 1340 °C, the value of $Q_u \times f$ was improved from 63,500 to 124,700 GHz. Increasing the sintering temperature above 1350 °C resulted in grain growth which was proven to be detrimental to the dielectric properties. The $Q_u \times f$ decreased when sintered above 1350 °C.

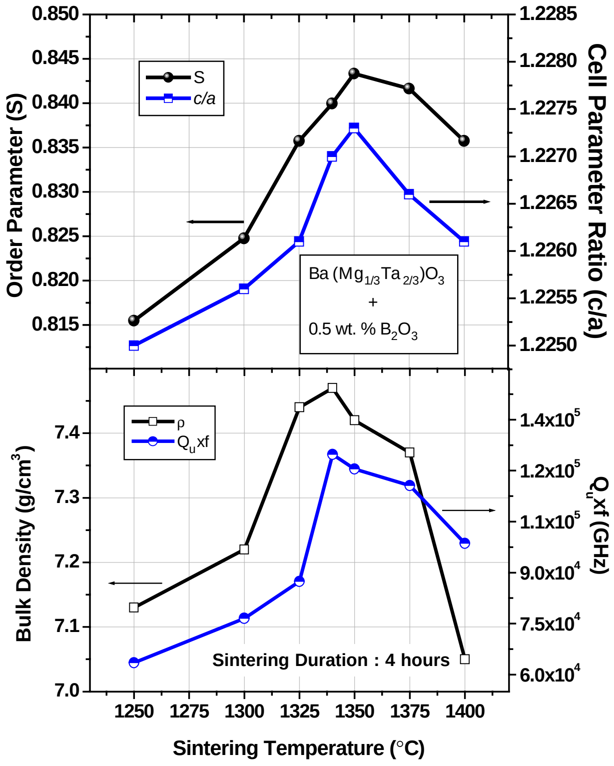


Fig. 1. The variation of bulk density, quality factor, cation ordering and unit cell parameter ratio of BMT added with 0.5 wt% of B_2O_3 with sintering temperature.

The effect of primary, secondary and ternary glasses on the processing temperature, densification and lattice parameters of BMT are given in Tables 2–4. In this investigation, it has been observed that addition of primary glasses like B_2O_3 up to 2 wt% can bring down the sintering temperature from 1625 to 1300 °C without appreciable deterioration in the microwave dielectric properties. The addition of silica glass did not result in appreciable lowering of the sintering temperature (see Table 2) may be due to the high melting point of SiO_2 (1600 °C). Moreover, doping of SiO_2 to a ceramic matrix may promote anomalous grain growth [34] which would result in porosity. In sodium borate glass, the basic structure contains chains of interlocking $BO_2(OH)$ triangles and $BO_3(OH)$ tetrahedrons bonded to chains of sodium and water octahedrons. Since the alkali ions are weakly held in the glassy network [35], its melting point is the lowest (75 °C) among the glass systems we have studied. Hence, the fluxing of BMT with sodium borate glass lowers the temperature to 1300 °C. However, it could not help in densifying the BMT ceramics may be because of its poor solubility in this glass. On the other hand in ternary glasses, it is generally agreed that large metal ions are held more firmly in the glass network [25]. The addition of ternary glasses did not reduce the sintering temperature to values less than 1300 °C (Table 4).

The theoretical density (D) of the BMT–glass ceramics is calculated using the following equation:

$$D_{\text{th}} = \frac{W_1 + W_2}{[W_1/D_1 + W_2/D_2]}, \tag{1}$$

where W_1 and W_2 are the weight percentage of the BMT matrix and glass with densities D_1 and D_2 in the mixture, respectively. The theoretical density of undoped BMT was calculated as 7.625 g/cm^3 using powder diffraction pattern of the sample sintered at 1650 °C and annealed at 1450 °C for 40 h. The green and sintered densities of various glass-added ceramic samples were given in Tables 2–4. A comparative study of the variation of green density with respect to additives revealed that maximum green density (above 65% of their respective theoretical densities) is observed for BMT doped with $PbO–B_2O_3–SiO_2$ glass which on sintering, resulted in a final densification of about 97% of their theoretical

Table 2
Sintering, densification and unit cell properties of BMT fluxed with primary glasses

BMT + glass	Wt% of additive	Sinter. temp. (°C)	Green density (g/cm^3)	Theor. density (g/cm^3)	Axial shrinkage	Radial shrinkage	Sintered density (g/cm^3)	c/a
B_2O_3	0.1	1375	4.974	7.609	72.3	82.2	7.480	1.2272
	0.2	1350	4.984	7.593	72.6	82.5	7.510	1.2268
	0.5	1350	4.981	7.546	72.0	81.6	7.441	1.2273
	1.0	1325	4.992	7.469	72.0	82.1	7.440	1.2270
	2.0	1300	4.989	7.323	74.2	83.4	7.200	1.2271
SiO_2	0.1	1500	4.452	7.619	73.1	83.7	7.390	1.2257
	0.2	1475	4.447	7.595	74.1	83.3	7.380	1.2251
	0.5	1460	4.436	7.552	74.5	84.6	7.301	1.2248
	1.0	1450	4.431	7.482	74.8	85.3	7.225	1.2246
	2.0	1450	4.430	7.396	75.1	86.8	7.015	1.2241

Table 3
Sintering, densification and unit cell properties of BMT fluxed with binary glasses

BMT + glass	Wt% of additive	Sintering temp. (°C)	Theor. density (g/cm^3)	Green density (g/cm^3)	% Axial shrinkage	% Radial shrinkage	Sintered density (g/cm^3)	c/a
B_2O_3–SiO_2	0.1	1370	7.597	4.484	73.0	82.2	7.394	1.2256
	0.2	1360	7.588	4.480	72.8	82.5	7.395	1.2252
	0.5	1360	7.534	4.522	72.7	81.6	7.350	1.2253
	1.0	1350	7.449	4.472	73.3	81.9	7.330	1.2251
	2.0	1340	7.284	4.470	73.7	83.5	7.281	1.2252
ZnO–B_2O_3	0.1	1420	7.617	4.823	72.1	82.7	7.429	1.2267
	0.2	1410	7.608	4.864	72.0	82.0	7.452	1.2267
	0.5	1410	7.583	4.855	72.5	82.6	7.444	1.2264
	1.0	1400	7.542	4.847	72.6	82.2	7.431	1.2256
	2.0	1375	7.462	4.825	74.2	85.3	7.421	1.2255
$5ZnO$–$2B_2O_3$	0.1	1400	7.606	4.872	73.3	82.8	7.438	1.2270
	0.2	1375	7.587	4.877	73.0	82.7	7.465	1.2271
	0.5	1360	7.532	4.868	72.5	82.5	7.496	1.2269
	1.0	1350	7.442	4.861	71.3	82.4	7.442	1.2272
	2.0	1330	7.271	4.862	71.5	82.4	7.270	1.2263
Al_2O_3–SiO_2	0.1	1475	7.610	4.751	73.5	83.5	7.417	1.2256
	0.2	1450	7.596	4.727	73.4	83.5	7.366	1.2255
	0.5	1440	7.552	4.732	73.5	84.7	7.285	1.2252
	1.0	1425	7.482	4.741	72.8	85.1	7.260	1.2253
	2.0	1420	7.347	4.740	71.5	86.6	7.157	1.2247
Na_2O–$2B_2O_3 \cdot 10H_2O$	0.1	1350	7.612	4.261	72.5	82.2	7.414	1.2252
	0.2	1325	7.599	4.272	72.4	82.0	7.302	1.2248
	0.5	1320	7.560	4.252	73.2	82.3	7.210	1.2241
	1.0	1310	7.497	4.248	73.7	82.9	7.070	1.2239
	2.0	1300	7.376	4.246	74.4	83.3	6.893	1.2220

densities. Doping with zinc borate glasses (ZnO–B_2O_3, $5ZnO$–$2B_2O_3$) also showed good green densities. The sintered density is maximum (98.7%) for 0.2 wt% B_2O_3-added ceramic. It should be noted that it is difficult to densify BMT more than 97% by conventional methods without the help of suitable dopants. It is well known that low contact angle, low dihedral angle and high solubility of the solid in the liquid are essential for achieving high sintered density in glass-added materials. In such cases, the transient glassy phase formed at a lower temperature would act as a short circuit medium for grain-to-grain materials transport [36]. The primary glass B_2O_3 is regarded as a typical glass network former that has a lower glass-transition temperature [37]. It is generally agreed that a nonwetting glassy network leads to porosity and hence the densification will be lower if the solubility of the ceramic in the liquid phase is poor. This could be the reason behind the poor densification of SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$ and $2MgO$–$2Al_2O_3$–$5SiO_2$. The percentage shrinkage along the axial and

Table 4
Sintering, densification and unit cell properties of BMT fluxed with ternary glasses

BMT + glass	Wt% of additive	Sintering temp. (°C)	Theor. density (g/cm^3)	Green density (g/cm^3)	Axial shrinkage	Radial shrinkage	Sintered density (g/cm^3)	c/a
$BaO–B_2O_3–SiO_2$	0.1	1390	7.615	4.414	72.3	82.5	7.402	1.2275
	0.2	1390	7.606	4.405	72.3	82.2	7.427	1.2266
	0.5	1380	7.578	4.395	72.7	81.3	7.424	1.2267
	1.0	1375	7.532	4.385	73.6	83.0	7.413	1.2267
	2.0	1350	7.444	4.392	74.6	83.3	7.402	1.2262
$MgO–B_2O_3–SiO_2$	0.1	1460	7.614	4.195	72.4	83.8	7.401	1.2278
	0.2	1430	7.606	4.202	72.3	83.6	7.419	1.2277
	0.5	1425	7.572	4.203	71.9	83.9	7.421	1.2274
	1.0	1425	7.521	4.198	72.9	82.6	7.426	1.2277
	2.0	1410	7.422	4.196	74.3	85.2	7.312	1.2272
$PbO–B_2O_3–SiO_2$	0.1	1410	7.619	5.050	72.9	83.4	7.411	1.2253
	0.2	1375	7.613	5.041	73.0	83.6	7.400	1.2262
	0.5	1335	7.596	5.124	72.4	83.8	7.381	1.2261
	1.0	1325	7.567	5.109	73.2	82.5	7.300	1.2268
	2.0	1300	7.511	5.104	73.5	82.7	7.224	1.2252
$ZnO–B_2O_3–SiO_2$	0.1	1375	7.616	4.277	71.6	82.3	7.399	1.2264
	0.2	1360	7.608	4.338	70.5	81.5	7.485	1.2265
	0.5	1335	7.583	4.361	72.3	82.4	7.484	1.2267
	1.0	1335	7.542	4.331	72.2	83.6	7.447	1.2270
	2.0	1330	7.461	4.361	73.4	83.7	7.403	1.2257
$2MgO–2Al_2O_3–5SiO_2$	0.1	1450	7.608	4.056	74.5	83.2	7.389	1.2253
	0.2	1435	7.589	4.158	74.7	82.4	7.341	1.2243
	0.5	1425	7.538	4.209	75.4	83.2	7.224	1.2244
	1.0	1410	7.454	4.201	75.7	83.3	7.152	1.2239
	2.0	1410	7.294	4.216	75.9	83.5	7.003	1.2241

radial directions is defined as

$$\text{Percentage shrinkage} = \frac{\text{Sintered dimension} \times 100}{\text{Green dimension}}, \quad (2)$$

which is given in Tables 2–4. It is expected that during sintering, the shrinkage along the axial component is more than that along the radial component. This is due to the gravitational effects which are more pronounced during liquid-phase sintering [38]. In liquid-phase sintering the densification occurs through the enhanced rearrangement of particles through low viscous liquid and eventually removes pores in the solid bodies. The evolution of the densification from green to sintered ceramic can be studied using a densification factor (DF) which is given by [39]

$$\mathrm{DF} = \frac{D_\mathrm{m} - D_\mathrm{g}}{D_\mathrm{th} - D_\mathrm{g}}, \quad (3)$$

where D_m is the measured sintered density, D_g the green density of the pressed compact, and D_th the theoretical density calculated by the mixing rule (Eq. (1)). Fig. 2 shows the variation of the densification factor as a function of the weight percentages of primary, binary and ternary glass additives in BMT. For primary glass additive B_2O_3, the DF increases first to 0.968 (for 0.2 wt% B_2O_3) from 0.93 (undoped BMT) and then decreased to 0.946 with higher additive concentration (for 2 wt% B_2O_3). On the other hand, the DF decreased with the SiO_2 addition. For zinc borate and borosilicate glasses the densification factor increases, while it decreased on aluminosilicate glass addition up to 0.5 wt% and then increases thereafter. A monotonous decrease of densification factor was observed for alkali borate glass addition. With exceptions of $PbO–B_2O_3–SiO_2$ and $2MgO–2Al_2O_3–5SiO_2$, the densification factor increased with additive concentrations (Fig. 2). Being a function of green density, slight errors in the measurement of green density can reflect in the calculated values of densification factor. So the anomalous variation of densification factor in the case of some glass additives need not always represent the sinterability of the glass ceramic. But, generally DF can be considered as a tool to test the wettability of the glass with the ceramic.

3.2. XRD analysis

It is known that BMT can exist in ordered and disordered forms. In the high-temperature-disordered phase, the Mg^{2+} and Ta^{5+} cations are randomly distributed on octahedral sites of the perovskite subcell which raises the symmetry of the system to cubic (cubic space group $Pm3m$). The ordering increases with the long-time annealing. In the low-temperature-ordered form (trigonal space group $P\bar{3}m1$) the Mg^{2+} and Ta^{5+}

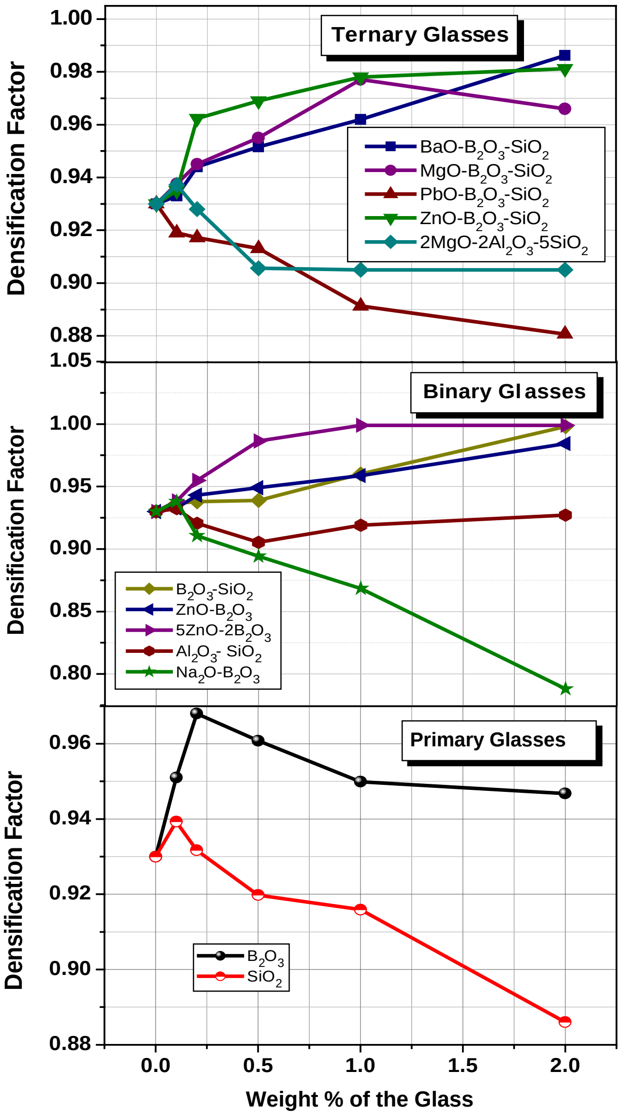


Fig. 2. The variation of the densification factor (DF) as a function of the weight % of the glass additives in primary, binary and ternary glasses.

cations are distributed on individual (111) planes of the perovskite subcell with alternating {Mg, Ta, Ta} layers. This is the 1:2 ordered configuration with the ordered phase is having a hexagonal superstructure. Prolonged annealing results in the expansion of the units cell along the (111) direction so that the unit cell parameter ratio (c/a) has a value greater than $\sqrt{\left(\frac{3}{2}\right)} = (1.2247)$. To quantitatively examine the degree of ordering, Matsumoto et al. [40] originally defined the order parameter for BMT using the following equation:

$$S = \sqrt{\frac{(I_{(100)}/I_{(110),(102)})_{\text{observed}}}{(I_{(100)}/I_{(110),(102)})_{\text{theoretical}}}}. \tag{4}$$

The theoretical value of the ratio of the integral intensity of super-structural reflection line (100) to that of (110,102) line, $(I_{100}/I_{110,102})_{\text{theoretical}}$ is 8.3% putting all the atoms in approximate ideal positions in BMT crystal lattice. Lu and Tsai [41] later modified this ratio to 8.14%. The accurate determination of the cation order factor must be done through Rietveld refinement technique [42] which is beyond the scope of this investigation. However, in real case where the structure factors of major reflections (which is a function of ions located in crystal structure) vary with slight deviations of cations from their ideal high-symmetry positions. The recent structural analysis carried out by Janaswamy et al. [43] and Lufaso [44] suggest that a more accurate value for $(I_{100}/I_{110,102})_{\text{theoretical}}$ which is equal to 8.7%. This value has been used for the determination of order parameter in this study.

Since the intensity of the ordering reflection line (100) is proportional to the difference in atomic scattering factors of Mg and Ta in complex perovskite BMT their intensities may be relatively lower. The ratio of the unit cell parameters (c/a) of BMT added with primary, binary and ternary glass systems are given in Tables 2–4. This investigation gave no evidence about the substitution of Zn, Al etc. ions from the glass at the Mg site in BMT. However, the XRD study cannot reveal any useful information when the substitution level is very small. But it has been revealed that certain glasses can control the order–disorder-phase transformation of BMT. The variation of the cation order parameter (S) with concentration of the glass addition is given in Fig. 3. The addition of 0.5 wt% of B_2O_3 increases the order parameter from 0.818 (undoped BMT) to 0.813. The ordering decreases to 0.837 on 2 wt% B_2O_3 glass addition. On the other hand, the cation ordering was severely damaged with SiO_2 addition. The c/a ratio also followed a trend similar to cation order parameter with glass incorporation (see Tables 2–4). For B_2O_3–SiO_2, Al_2O_3–SiO_2 and Na_2O–$2B_2O_3 \cdot 10H_2O$ the order parameters decreased with glass addition, while for zinc borate glasses (ZnO–B_2O_3 and $5ZnO$–$2B_2O_3$) the cation ordering increased for small amount of glass content and then decreased with higher concentration. In the case of ternary glass systems, except BaO–B_2O_3–SiO_2 and $2MgO$–$2Al_2O_3$–$5SiO_2$ the cation ordering of BMT increased with an increase in glass content up to 1 wt% and then decreased (Fig. 3).

A number of investigators established [45,46] that formation of satellite secondary phases such as $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, $BaTa_2O_6$, etc. during solid-state synthesis of BMT, are detrimental to its densification, cation ordering and microwave dielectric properties. Fig. 4 shows the powder diffraction profiles of 0.5 wt % B_2O_3-added BMT calcined at 1200 °C and sintered at temperatures 1250, 1300, 1325, 1340, 1350, 1375 and 1400 °C. Many investigators analyzed the solid-state reaction mechanism of BMT which is reported to be highly complex. Fang et al. [47] reported that $BaTa_2O_6$

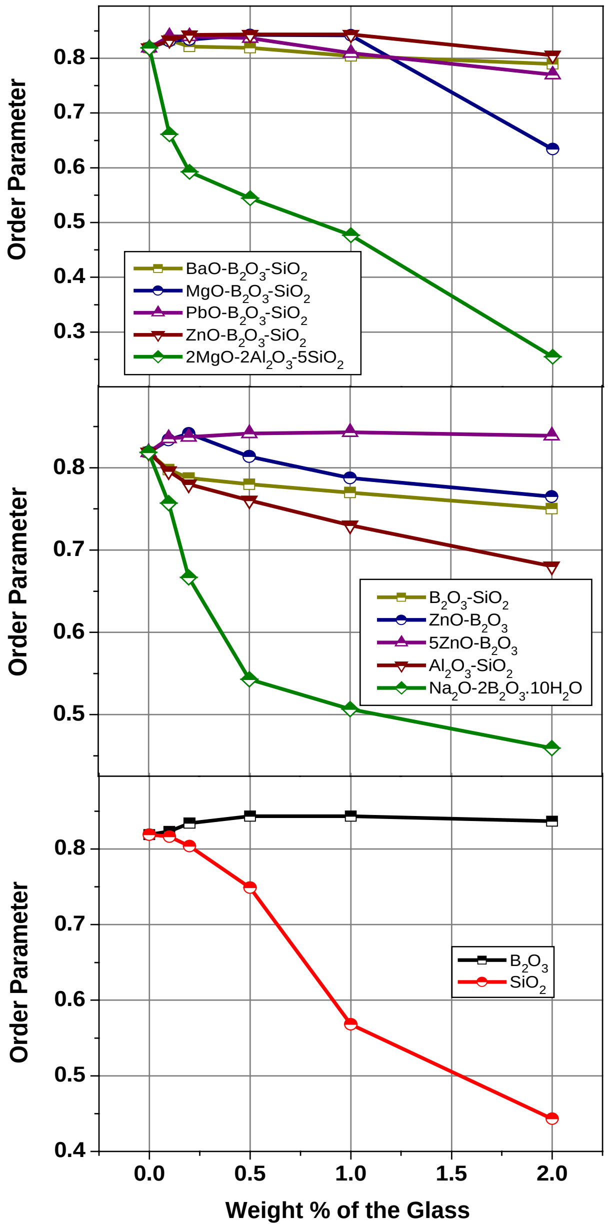


Fig. 3. The variation of the cation ordering parameter (S) as a function of the weight % of the glass additives in primary, binary and ternary glasses.

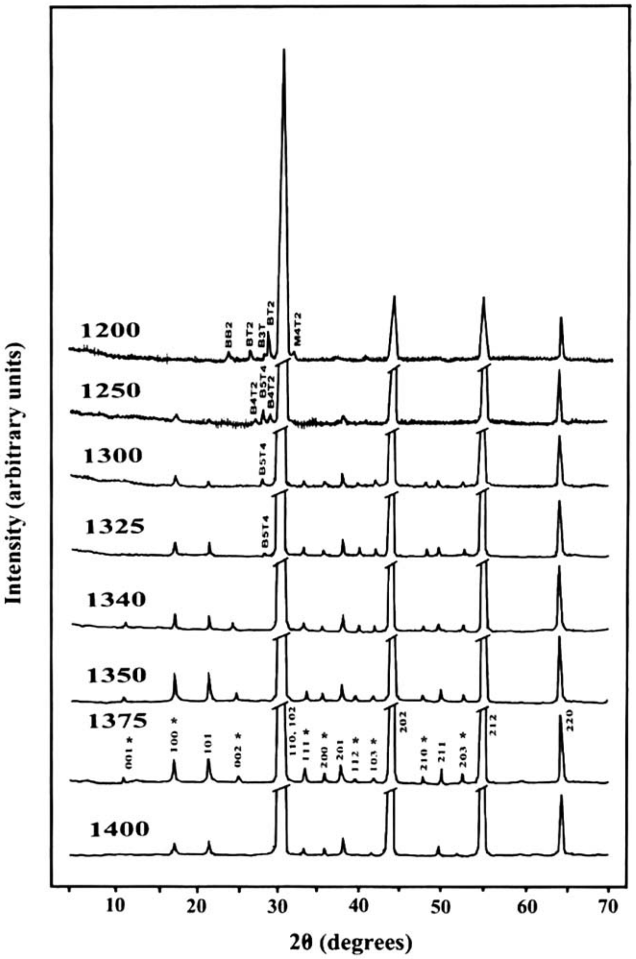


Fig. 4. Powder diffraction patterns of BMT doped with 0.5 wt% of B_2O_3 glass at various sintering temperatures (∗ represent superstructure reflections). The abbreviations stand for BB2–BaB_2O_4, BT2–$BaTa_2O_6$, M4T2–$Mg_4Ta_2O_9$, B3T–$Ba_3TaO_{5.5}$, B4T2–$Ba_4Ta_2O_9$, B5T4–$Ba_5Ta_4O_{15}$.

and $Ba_4Ta_2O_9$ are the two intermediate phase resulting from the reaction between $BaCO_3$ and Ta_2O_5. In principle, they on reaction with MgO forms the desired end compound BMT. However, in a previous report the same authors cautioned [48] that there are chances when these two intermediates react each other to form $Ba_5Ta_4O_{15}$ and $Ba_7Ta_6O_{22}$. From $Ba_5Ta_4O_{15}$ and $Ba_7Ta_6O_{22}$, it is very difficult to form BMT because the reactants are stable even at high temperature and the reaction needs to occur through a solid-state diffusion process. The mechanism for these reactions is not clear; however, it is reasonable to assume that they have to make contact with MgO to form BMT by long-distance diffusion. If these two compounds are formed in the precursor powder during the calcination processes, they will maintain growth during sintering and finally present as secondary phases in the sintered body.

The XRD pattern recorded from samples sintered at 1200 °C suggested that with addition of 0.5 wt% B_2O_3 into the matrix, satellite phases such as $BaTa_2O_6$, $Ba_3TaO_{5.5}$ and $Mg_4Ta_2O_9$ were detected in the samples in small amounts (Fig. 4). These phases might have formed as a result of an incomplete solid-state reaction when the samples were calcined at 1200 °C. At still higher temperatures, the phases such as $BaTa_2O_6$ could be transformed into the desired BMT or could remain in the samples as additional phase, which in turn can decrease the dielectric *Q* factor of the material. It is expected that the possible formation of the transient liquid phases like BaB_2O_4 might have helped the materials transport. However, such a phase was not detected in the present XRD profile. When the samples were sintered at 1250 °C, the additional phases formed were $Ba_5Ta_4O_{15}$ and $Ba_4Ta_2O_9$. Apart from these, the samples revealed an ordered perovskite structure with superstructure reflections visible in the XRD pattern. At 1325 °C, the XRD profile represented only single-phase BMT with no trace of additional phases like $Ba_5Ta_4O_{15}$. This indicates that in presence of a vitreous medium, stable phases like $Ba_5Ta_4O_{15}$ can react with MgO to form stable BMT which is very difficult to occur in ordinary high-temperature solid-state reaction synthesis [45]. Sintering at higher temperatures retains the ordered structure, but the bulk density decreases which can be due to grain growth (Fig. 1). Furthermore, this observation confirms a recent finding by Cheng et al. [22] that the presence of satellite phases in BMT can be eliminated by glass fluxing. It must be noted that even for higher percentage of B_2O_3 addition no traces of glassy phases noticed in the XRD. This confirms the volatization of B_2O_3 at high temperatures after the formation of a transient vitreous phase which enables efficient particle rearrangement and material transport during sintering. It is also evident that order parameter (S) and the unit cell parameter ratio (c/a) of BMT doped with 0.5 wt% B_2O_3 glass were increased with sintering temperature and approached its maximum value at 1350 °C. Increasing the sintering temperature above 1350 °C deteriorated the cation ordering (see Fig. 1 and Table 2). A similar observation regarding the suppression of barium tantalate phases were observed with other glass systems like $5ZnO–2B_2O_3$ and $ZnO–B_2O_3–SiO_2$ (the XRD profiles are not given here). It was also observed that with 0.5 wt% $PbO–B_2O_3–SiO_2$ glass fluxing, a small trace of $Ba_7Ta_6O_{22}$ was noticed in their respective powder patterns besides the usual $BaTa_2O_6$. The diffraction peaks of $Ba_7Ta_6O_{22}$ and $BaTa_2O_6$ disappeared on the addition of 1 mole% of $PbO–B_2O_3–SiO_2$ glass.

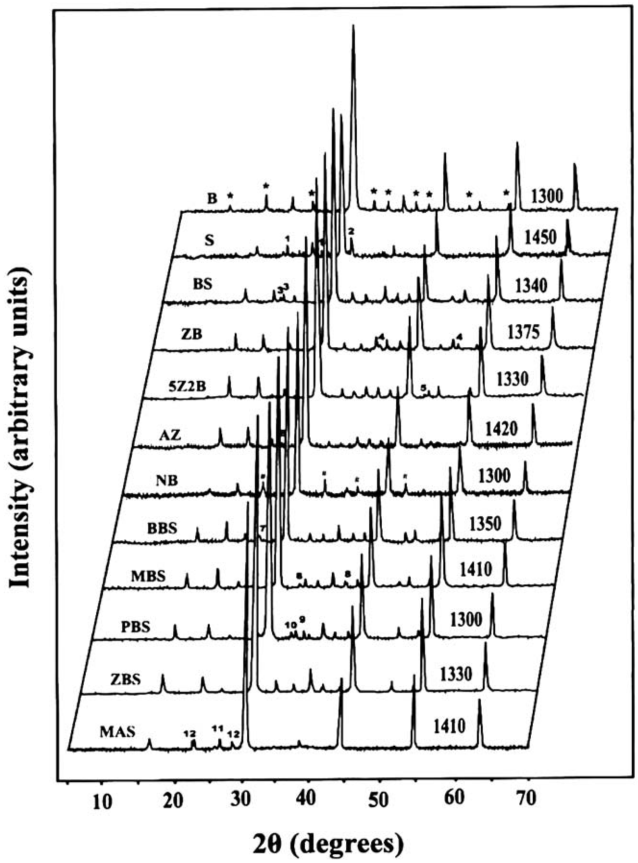
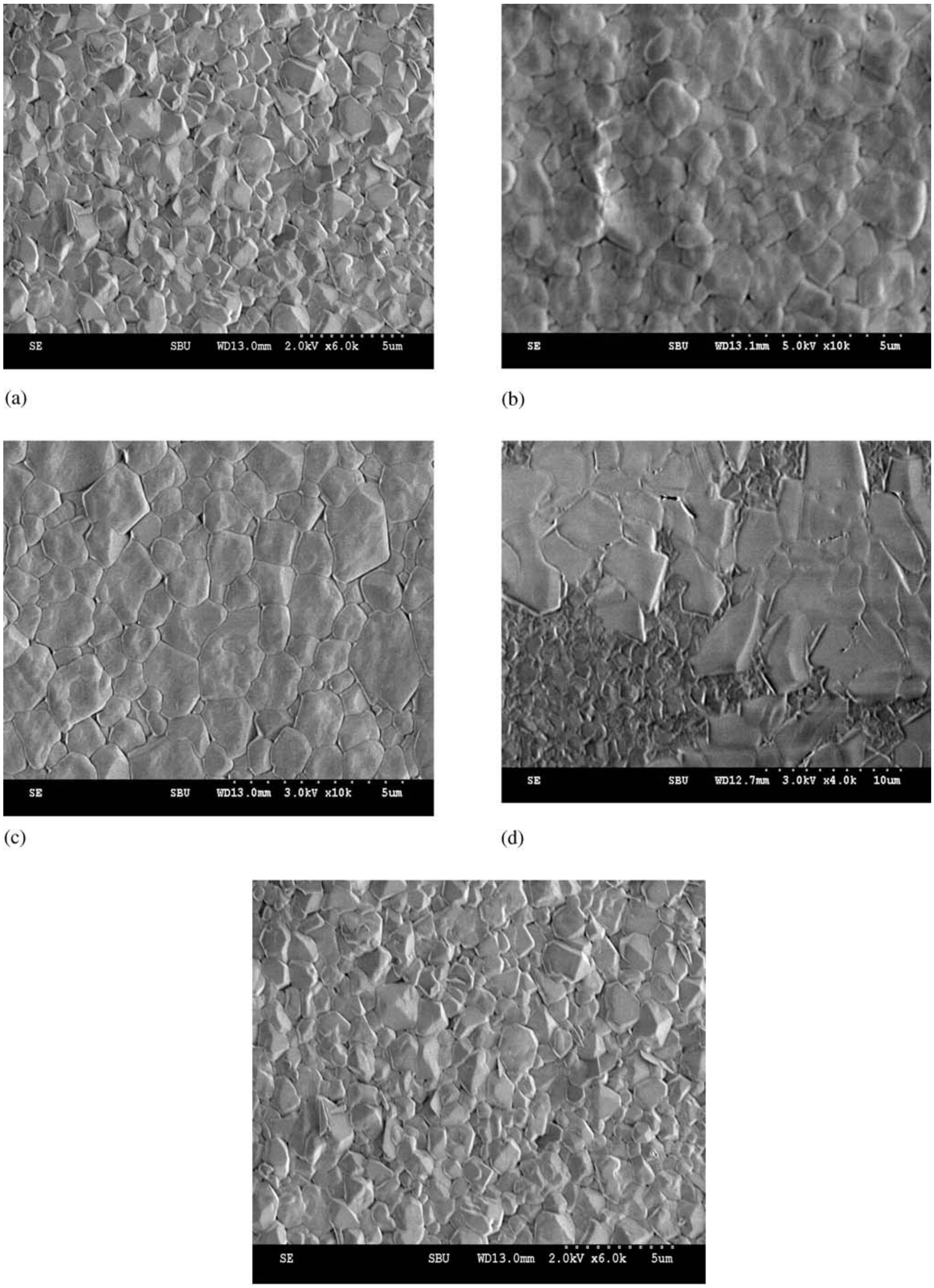


Fig. 5. Powder diffraction pattern of BMT doped with 2 wt% of various glasses (∗ represent superstructure reflections and # represent unidentified peaks). The peak numbers stand for (1) $Ba_3Si_5O_{13}$, (2) $MgSiO_3$, (3) B_2SiO_5, (4) $Zn(BO_2)_2$, (5) β-$Zn_5B_4O_{11}$, (6) Al_2SiO_5, (7) $Ba_3B_6Si_{12}O_{16}$, (8) $Mg_3(BO_3)_2$, (9) $Pb_5Si_2O_7$, (10) PbB_4O_7, (11) $BaMgSi_4O_{10}$ and (12) $Mg_2Al_4Si_5O_{18}$.

Fig. 5 describes the XRD patterns recorded from BMT fluxed with 2 wt% different glasses. It is observed that addition of certain glasses of about 2 wt% gave rise to a number of additional phases formed may be due to the decomposition of some glasses at high temperatures and their consequent reaction with the matrix phase. The slow cooling (60 °C per hour) of the glass ceramic after sintering could lead to the formation of these crystalline phases. Doping up to 0.5 wt% primary glasses like B_2O_3 will not form any additional phase but will act as a sintering aid. Addition of B_2O_3 glass in excess of 2 wt% will result in the formation of BaB_4O_7 (JCPDS File Card. No. 15-862) secondary phases and decreased the dielectric Q factor. No additional phases were observed when the samples were sintered at 1300 °C (see Fig. 5). As the concentration of SiO_2 in BMT increases, additional lines corresponding to $Ba_3Si_5O_{13}$ (JCPDS File Card. No. 26-179) and a weak line for $MgSiO_3$ (19-768) appeared in the powder diffraction profile. The crystalline phase of borosilicate glass (B_2SiO_5, JCPDS Card. No. 42-392) was visible in the XRD pattern of BMT (Fig. 5) doped with 2 wt% $B_2O_3–SiO_2$. The two diffraction peaks for $Zn(BO_2)_2$ (Card. No. 39-1126) and β-$Zn_5B_4O_{11}$ (Card. No. 9-153) were appeared in their respective powder diffraction patterns when BMT is doped with them up to 0.5 wt%. But no such additional peaks are visible when the samples are doped up to 2.0 wt% (see Fig. 5 and SEM picture Fig. 6(b)). Formation of crystalline Al_2SiO_5 (Card. No. 38-471) may be the reason for the decrease of density for higher concentration of $Al_2O_3–SiO_2$-doped samples. It is also observed that addition of borax glass ($Na_2O–2B_2O_3 \cdot 10H_2O$) severely damaged the cation ordering of BMT and powder diffraction patterns presents no superstructure reflection peaks when the ceramic is doped with it in excess of 2.0 wt%. A few unidentified additional diffraction lines were present in the profile which could not be indexed using any of the standard schemes of indexing. This observation was



(a) (b) (c) (d) (e)

Fig. 6. The scanning electron micrographs of BMT. (a) Doped with 0.1 wt% B_2O_3 sintered at 1375 °C, (b) doped with 2 wt% of $5ZnO–2B_2O_3$ sintered at 1375 °C, (c) doped with 2 wt% of $ZnO–B_2O_3–SiO_2$ sintered at 1330 °C, (d) doped with 2 wt% of $PbO–B_2O_3–SiO_2$, sintered at 1300 °C and (e) undoped BMT sintered at 1350 °C.

consolidated by the low value of the cation order parameter (0.459) (Fig. 3). The addition of ternary glasses resulted in the formation of a number of additional lines. When BMT was fluxed with 0.1 wt% of $BaO–B_2O_3–SiO_2$ a small diffraction line corresponding to $BaSi_4O_9$ (Card. No. 15-386) appeared in the XRD pattern (Fig. 5) which could be the reason behind the anomaly in its dielectric constant. Doping of BMT with more than 0.2 wt% of $BaO–B_2O_3–SiO_2$ resulted in the formation of $Ba_3B_6Si_{12}O_{16}$ (Card. No. 6-351). Even a small concentration of $MgO–B_2O_3–SiO_2$ resulted in the formation of $Mg_3(BO_3)_2$ (Card. No. 33-858) whose intensity was diminished with more MBS concentration. This is suspected to be due to the evaporation of the glass during sintering or the reaction with the matrix resulted in the formation of some unidentified phase whose presence could not be detected by XRD. Glass fluxing of BMT with 1 wt% PBS gave rise to $Pb_5Si_2O_7$ phase (Card. No. 32-538) while with 2 wt%, an additional phase of PbB_4O_7 (Card. No. 15-278) also appeared in the XRD pattern. The doping with $ZnO–B_2O_3–SiO_2$ seems to be most interesting as the formation of the additional phases were not visible in the XRD profiles. For 0.1 wt% a small trace of Zn_2SiO_4 (Card. No. 24-1467) was detected in the XRD but the additional phase disappears with more addition of $ZnO–B_2O_3–SiO_2$. The formation of secondary phases such as $BaMgSi_4O_{10}$ (Card. No. 15-799) was detected at a doping level of 1.0 wt% $2MgO–2Al_2O_3–5SiO_2$. One more additional line of crystalline cordierite, $2MgO–2Al_2O_3–5SiO_2$ (Card. No. 13-293) has appeared in the XRD pattern of BMT doped with cordierite up to 2 wt% (see Fig. 5). This result confirms a recent finding by Cheng et al. [22] who observed that excess presence of cordierite in BMT hindered its densification process and thereby deteriorated the microwave dielectric properties.

It is likely that on doping with zinc and aluminum-based glasses, a small amount of ions like Zn^{2+} and Al^{3+} can substitute the Mg site in BMT due to their comparable size and charge. It is also possible that small amount of sodium in borax glass can go into the Ba^{2+} site of BMT. But the conventional XRD analysis based on powder diffraction methods does not give any information for such a very small amount of substitutions.

3.3. Microstructural analysis

The scanning electron micrographs recorded from a few typical samples were presented in Fig. 6. Fig. 6(a) is the electron micrograph of BMT sample doped with 0.1 wt% of B_2O_3 which was sintered at 1375 °C. The average grain size was about 1 μm. The SEM picture did not show the presence of any additional phases. This may be either due to (i) the amount of glass content was too negligible to be detected or (ii) since the liquid-phase sintering is a transient phenomenon, the B_2O_3 melt might have evaporated away after acting as an effective medium for molecular diffusion. Some previous reports [15] on the effects of B_2O_3 in $Ba_2Ti_9O_{20}$, also confirmed that B_2O_3 is volatile during the high temperature sintering above 1200 °C. Fig. 6(b) gives the surface morphology of BMT doped with 2 wt% of $5ZnO–2B_2O_3$. Here, SEM picture showed closely packed grains. The formation of the low melting-phase β-$Zn_5B_4O_{11}$ has enhanced the densification of BMT by providing a liquid-phase medium. The addition of $ZnO–B_2O_3–SiO_2$ glass has enhanced the densification phenomena through enhanced material transport, as it is clear from Fig. 6(c). In this case the friction between the particles during diffusion was significantly reduced. So they can rearrange easily under the action of the compressive stress exerted by the liquid. It should be noted that the diffusion through a liquid is more efficient than a solid. The melted phase of $PbO–B_2O_3–SiO_2$ glasses is visible in Fig. 6(d) which is the micrograph of BMT fluxed with 2.0 wt% of $PbO–B_2O_3–SiO_2$, sintered at 1300 °C. The XRD analysis suggests that the additional liquid phase may be either $Pb_5Si_2O_7$ or PbB_4O_7 or a homogeneous mixture between them. Fig. 6(e) show the SEM picture of pure BMT ceramic sintered at 1350 °C without additives showing a highly porous structure.

3.4. Microwave dielectric properties

The glass-assisted sintered ceramics need not necessarily result in the desired improvement in dielectric properties. This is especially true if the dielectric constant and Q factor of the matrix material are lowered by the presence of a continuous low dielectric constant grain boundary phase. To tackle this problem one need to control the grain growth related porosity consequent to glass fluxing and reduce the volume fraction of the low dielectric constant secondary phases formed as a result of the reaction of the vitreous phase with the ceramic. The glass can act either as a fluxing agent for liquid-phase sintering or a modifier of the dielectric properties if the glass component is incorporated into the lattice of the ceramic matrix [49]. Therefore the suitable composition of the glass additive and the chemical interaction of the BMT with glasses are important aspects in understanding, characterizing and controlling their dielectric properties.

3.4.1. Primary glasses

The microwave dielectric properties of undoped BMT with a densification of 93.1% of the theoretical density are $\varepsilon_r = 24.8$, $\tau_f = 8\,ppm/°C$ and $Q_u \times f = 80{,}000\,GHz$. This sample was sintered at 1600 °C for 4 h in air. We have also observed [50] that increasing the sintering temperature up to 1650 °C or prolonged annealing up to 40 h at 1450 °C could increase densification up to 97.5% and $Q_u \times f$ to 125,300 GHz. It is worthwhile to note that the doped ceramic samples used in this investigation was not annealed. This is because the sintering temperatures of most of the glass-fluxed BMT ceramics were less than 1400 °C while the usual annealing temperature of BMT was 1450–1500 °C. In order to promote cation ordering in complex perovskite BMT the sintered samples were subjected to a very slow cooling rate (1 °C/min). Fig. 7 gives the microwave dielectric properties of B_2O_3 and SiO_2 glass-added BMT. The dielectric constant increased from 24.8 (pure BMT) to 25.0 when the sample was added with 0.2 wt% of boric oxide and further addition resulted in a decrease of it. On the other hand, the ε_r was considerably decreased with SiO_2 addition.

The temperature coefficients of resonant frequency (τ_f) and dielectric constant (τ_ε) are related by the relation,

$$\tau_f = -(\tau_\varepsilon/2 + \alpha_T), \tag{6}$$

where α_T is the thermal expansion coefficient of the glass–ceramic composite. In amorphous materials the dielectric constant increased with temperature due to the relatively weak bonding structure. With a finite value of the thermal expansion coefficient the τ_ε will have high positive values which eventually makes τ_f of most of the glassy materials negative [27]. The τ_f of BMT decreases with B_2O_3 and SiO_2 addition, approached more negative values when doping level of the glass exceeded. It is interesting to note in Fig. 7 that τ_f was close to zero (+2.4 and −1.3 ppm/°C respectively) for samples mixed with 0.5 and 1.0 wt% of B_2O_3.

The quality factor of BMT increased for small amounts of B_2O_3. For 0.5 wt% of B_2O_3 addition $Q_u \times f$ reached 124,700 GHz. The unloaded quality factor decreased with further addition of B_2O_3 glass where the densification factor also followed a similar trend (see Fig. 2). The effect of SiO_2 glass in BMT on the other hand destroyed its cation ordering (see Table 2) and severely deteriorated the microwave quality factor (Fig. 7).

3.4.2. Binary glasses

The variation of the dielectric properties of BMT as a function of weight percentage of the binary glass additives is given in Fig. 8. In the case of binary systems like $5ZnO–2B_2O_3$, $ZnO–B_2O_3$ and $B_2O_3–SiO_2$, the dielectric constant which is an indicator of the various polarization phenomena of the ceramic, increases slightly with glass addition. On adding 0.5 wt% of $5ZnO–2B_2O_3$ glass, the measured values of ε_r increased to 25.4 and then gradually decreased to 24.5 with 2.0 wt% of the additive. The maximum values of ε_r for BMT doped with $B_2O_3–SiO_2$ and $ZnO–B_2O_3$ were 25.1 and 25.3 for 0.1 and 0.2 wt% of the additives, respectively. For all other binary glasses the dielectric constant decreased with increasing concentration of the glass additive. For sodium diborate decahydrate glass, the lowest value of dielectric constant was observed as 16.4 (for 2 wt% of the $Na_2O–2B_2O_3 \cdot 10H_2O$). It is worthwhile to note that the behavior of dielectric constants of the glass-fluxed ceramics do not exhibit any direct relationships with the intrinsic dielectric properties of the glass systems (Table 1).

Unlike primary glasses, anomalous behavior of τ_f is observed when BMT is doped with binary glass compositions. In the case of borosilicate glass, the τ_f increased with glass content and approached values as high as +33.6 ppm/°C (for 2.0 wt% $B_2O_3–SiO_2$) while for the same concentration of aluminosilicate it is 14.8 ppm/°C. For very small amount of $ZnO–B_2O_3$, the τ_f has negative values while it increased to 9.8 ppm/°C with 2.0 wt% glass addition. The τ_f first decreased to 3.4 and then increased to 14 ppm/°C with aluminosilicate glass doping. The irregular variation of τ_f in some glass-added ceramics are attributed to the formation of additional phases formed as a result of the reaction of the glass with BMT matrix. In the case of sodium borate addition, the τ_f of BMT showed negative values (see Fig. 8). Among binary glass compositions, the temperature coefficient of resonant frequency showed steady values only in the case of $5ZnO–2B_2O_3$ addition.

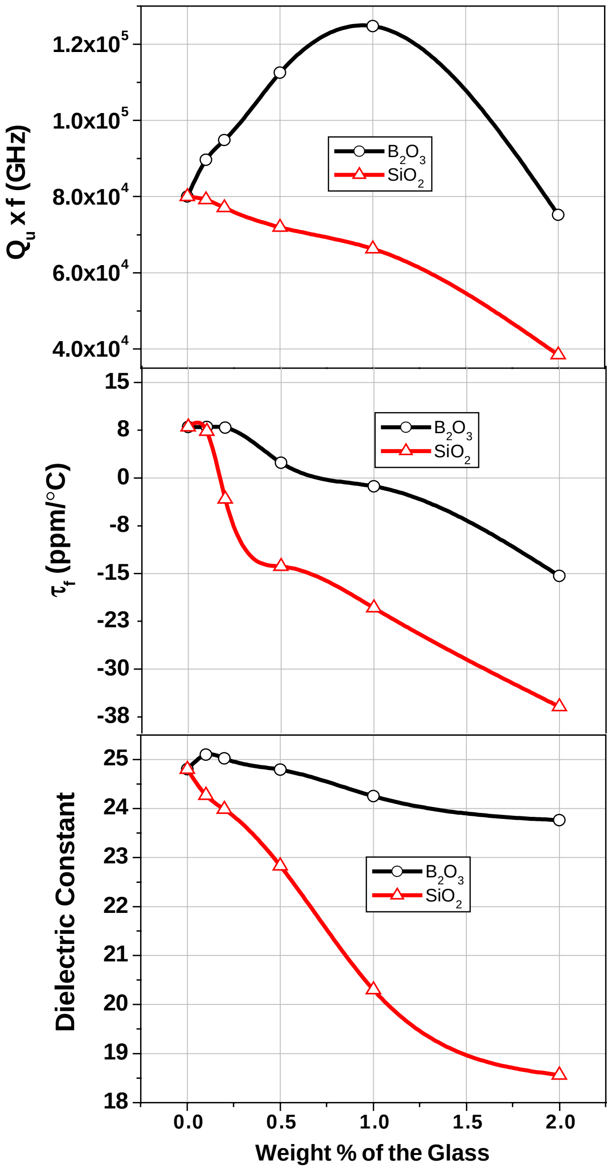


Fig. 7. Variation of microwave dielectric properties of BMT as a function of primary glass addition.

The unloaded quality factor of BMT increased to $Q_u \times f = 136{,}500$ GHz with 0.2 wt% of $ZnO–B_2O_3$ addition. With small amount of $Al_2O_3–SiO_2$ addition a slight

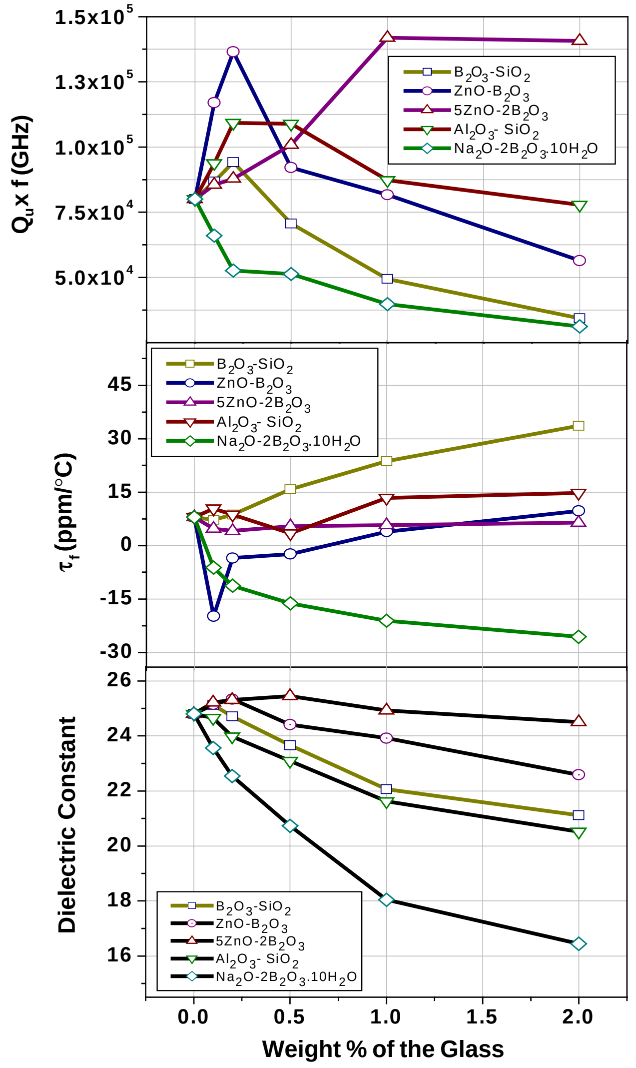


Fig. 8. Variation of microwave dielectric properties of BMT as a function of binary glass addition.

improvement of microwave quality factor ($Q_u \times f = 109{,}200$ GHz) was observed. It is interesting to note that the quality factor of BMT increased steadily with 5ZnO–$2B_2O_3$ content. It is believed that the formation of the low melting β-$Zn_5B_4O_{11}$ has been beneficial to the materials transport mechanism in these glass-fluxed ceramics. The best microwave property among binary glass-added BMT ceramic was recorded for 1.0 wt% 5ZnO–$2B_2O_3$ addition where the $Q_u \times f$ was 141,800 GHz. The addition of alkali glass was found to deteriorate the microwave dielectric properties of BMT ceramics. The XRD studies revealed the presence of unidentified compositions. In alkali borate glass [25], the oscillation of the alkali ion was limited by crystal bonding while in the vitreous state they were loosely held in the interstices of the glassy network which were relatively free to oscillate with external field. This can lead to extensive dielectric losses. When such lossy amorphous material was incorporated into the low-loss BMT, the dielectric loss quality of the latter can increase.

3.4.3. Ternary glasses

The influence of the additional satellite phases formed consequent to the interaction of the glass with the ceramic matrix played a significant role in controlling the microwave dielectric properties of the ternary glass-fluxed BMT. The evolution of the dielectric properties of BMT added with ternary glass compositions are given in Fig. 9. For glass systems like BaO–B_2O_3–SiO_2, ZnO–B_2O_3–SiO_2 and 2MgO–$2Al_2O_3$–$5SiO_2$ the dielectric constant slightly increases for small values of the glass content and then decreases as the presence of glass in the

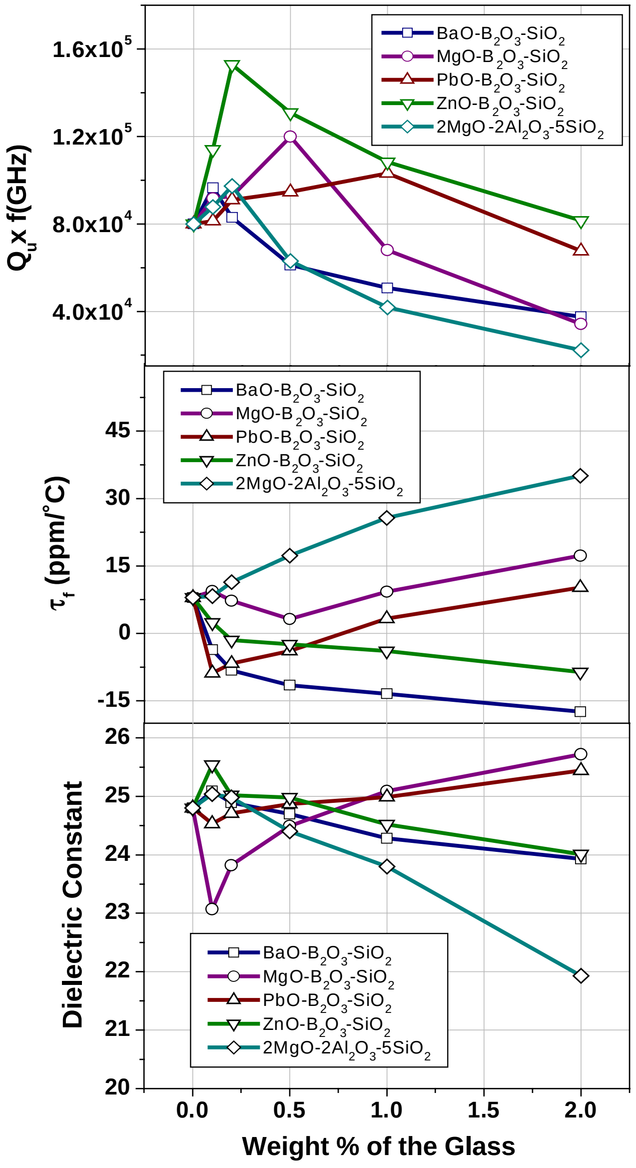


Fig. 9. Variation of microwave dielectric properties of BMT as a function of ternary glass addition.

mixture increases. But the percentage decrease in ε_r is more for cordierite glass which can be due to the formation of additional phases such as $BaMgSi_4O_{10}$. For $MgO–B_2O_3–SiO_2$ addition, ε_r decreased to 23.0 with 0.2 wt% of the glass due to the formation of $Mg_3(BO_3)_2$ phase and then increased. In the case of $PbO–B_2O_3–SiO_2$ doping also, the dielectric constant decreased slightly which may be due to the formation of $Pb_5Si_2O_7$ and PbB_4O_7 phases.

The temperature coefficient of resonant frequency of the glasses decreased from 8 to -17.4 ppm/°C for $BaO–B_2O_3–SiO_2$ and to -8.6 ppm/°C for $ZnO–B_2O_3–SiO_2$ when they were added up to 2 wt%. A minimum τ_f value of 1.3 ppm/°C has been found in 1.0 wt% of $PbO–B_2O_3–SiO_2$ glass mixed BMT. It has already been reported [27] that the temperature coefficient of all these glasses were negative. The $MgO–B_2O_3–SiO_2$-fluxed BMT showed an initial dip in the τ_f values which may be due to the presence of $Mg_3(BO_3)_2$ secondary phase. It is interesting to note that a similar anomaly has been observed in the variation of dielectric constant of BMT with $MgO–B_2O_3–SiO_2$ glass incorporation. The temperature coefficient of resonant frequency of cordierite ($Mg_2Al_4Si_5O_{18}$)-doped BMT was positive and increased with increasing amount of cordierite. This is surprising since cordierite is reported [53] to have a negative τ_f.

The unloaded quality factor of 0.2 wt% $ZnO–B_2O_3–SiO_2$ glass-added BMT was around $Q_u \times f =$ 152,800 GHz. This result is most interesting as it revealed that this ternary glass system provides an ideal wetting medium for the liquid-phase sintering of complex perovskite BMT. The XRD patterns showed no additional peaks except superstructure reflections representing an ordered crystal structure formed with cation order parameter 0.843 (Fig. 3). There has been similar reports about the ideal wetting characteristics of $ZnO–B_2O_3–SiO_2$ with other low-loss ceramics like [51] TiO_2 and [20] $MgTiO_3–CaTiO_3$. It must be noted that the addition of other ternary additives also resulted in an increase in the $Q_u \times f$ value from 80,000 GHz (of pure unannealed BMT). The best quality factors measured with the addition of other ternary glass dopants were given by $Q_u \times f = 96{,}500$ for $BaO–B_2O_3–SiO_2$ (0.2 wt%), 119,900 for $MgO–B_2O_3–SiO_2$ (0.5 wt%), 103,100 for $PbO–B_2O_3–SiO_2$ (1.0 wt%) and 97,300 for $2MgO–2Al_2O_3–5SiO_2$. The microwave quality factor of most of the glass-added dielectrics decreased when the doping level of the glass increased due to the formation of the satellite phases formed. It is worthwhile to remember that Cheng et al. [22] made a similar observation, who attributed the poor performance of dielectric properties of BMT fluxed with $MgO–CaO–SiO_2–Al_2O_3$ (MCAS) was probably due to the decomposition of MCAS glass into cordierite phase which can eventually damage the microwave quality factor of the ceramic. In general, in glasses the main cause of dielectric loss is associated with deformation loss mechanism [27] and introduction of a lossy glass into the ceramic may aggravate the loss of the ceramic.

In a previous report, Ra et al. [54] suggested that *B*-site cation ordering is not the primary factor that influences the observed microwave dielectric loss in BMT. They attributed dielectric loss of this ceramic to the atomic level point defect induced from raw material impurities, processing etc. The variation of the cation order factor and unloaded quality factor of three typical glasses such as B_2O_3 (primary), $5ZnO–2B_2O_3$ (binary) and $ZnO–B_2O_3–SiO_2$ (ternary) are plotted in Fig. 10. Since the variation of the quality factor and cation order

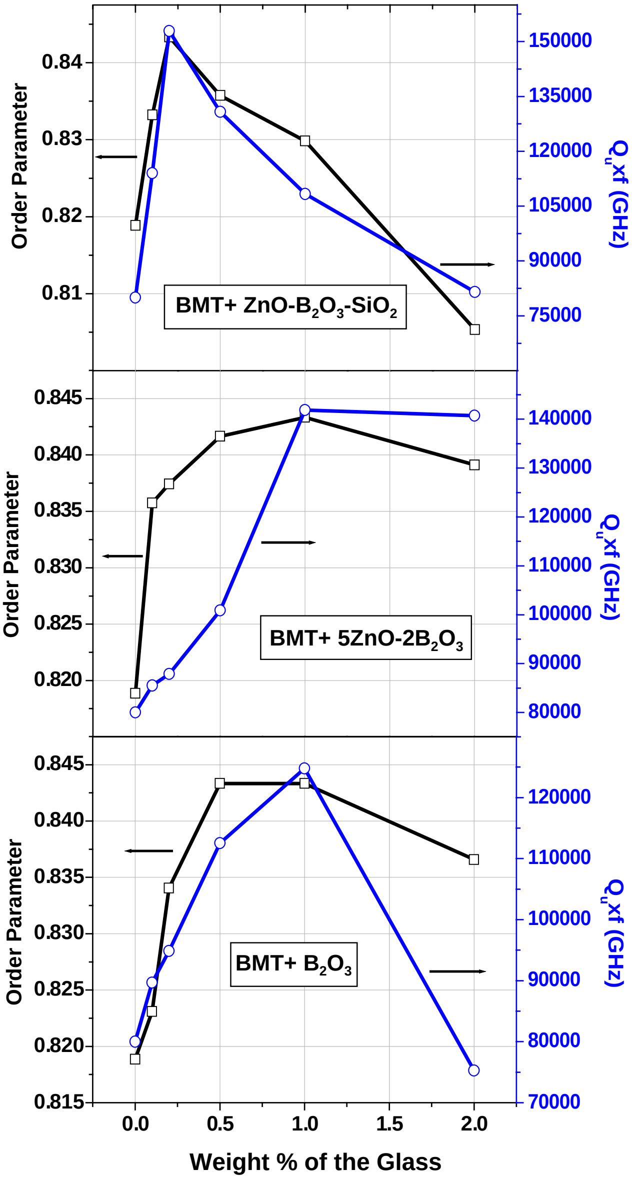


Fig. 10. Variation of unloaded quality factor and ordering parameter of BMT doped with B_2O_3, $5ZnO–2B_2O_3$ and $ZnO–B_2O_3–SiO_2$ as a function of weight percentage of the additive.

parameter follows a more or less similar trend within the limits of experimental error, it is evident that *B*-site cation ordering of Mg^{2+} and Ta^{5+} is the fundamental requirement for high quality factor in complex perovskite BMT ceramics. Moreover, this result gives justification to the procedure of calculation of order parameter using Eq. (4) which use the ratio of intensity of superstructure (100) line and fundamental reflection (110,102).

It must be remembered that the reduction in sintering temperature in this research report was not sufficient enough for applications in multilayer structures using LTCC technique where the sintering temperature must be less than 961 °C which is the melting point of silver electrode. Furthermore, the amount of liquid-phase content was not adequate for complete liquid-phase sintering to occur. But in most of the advanced ceramics, the amount of liquid phase produced at the time of firing is kept typically below 5 vol% to safeguard the physical or electrical properties from deterioration as a result of additional phase formation at the grain boundaries [37]. The present investigation is useful in selecting the right glass compositions that aid vitreous sintering in complex perovskite BMT ceramics.

4. Conclusion

The liquid-phase sintering aspects of complex perovskite BMT is investigated. Different weight percentage of glasses such as B_2O_3, SiO_2, B_2O_3–SiO_2, ZnO–B_2O_3, 5ZnO–$2B_2O_3$, Al_2O_3–SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$, BaO–B_2O_3–SiO_2, MgO–B_2O_3–SiO_2, PbO–B_2O_3–SiO_2, ZnO–B_2O_3–SiO_2 and 2MgO–Al_2O_3–$5SiO_2$ were added to calcined BMT precursor. The effect of glass fluxing on the phase evolution, densification, cation ordering, microstructure and microwave dielectric properties of BMT is investigated.

- In conventional solid-state synthesis, sintering at high temperatures 1625–1675 °C for several hours and annealing up to several days are needed to stabilize the ordered high *Q* phase of BMT ceramics. The sintering temperature of BMT ceramics was reduced to about 1300 from 1650 °C with glass additives. The BMT ceramics when doped with glass systems such as B_2O_3, ZnO–B_2O_3, 5ZnO–$2B_2O_3$ and ZnO–B_2O_3–SiO_2 and sintered in the temperature range 1300–1450 °C showed ordered perovskite structure without any annealing. Thus the cost of production of BMT can be reduced by using glass additives without any deterioration in the microwave dielectric properties.
- Best densification of about 98.7% of the theoretical density was observed for B_2O_3-added ceramics. Reasonably good densification was observed for ZnO–B_2O_3–SiO_2, 5ZnO–$2B_2O_3$ glass additives. Densification of BMT was poor with SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$ and 2MgO–$2Al_2O_3$–$5SiO_2$ glass additions.
- Glass addition suppressed the formation secondary phases such as $Ba_5Ta_4O_{15}$ and $Ba_7Ta_6O_{22}$. A small amount of glass additive such as B_2O_3, ZnO–B_2O_3, 5ZnO–$2B_2O_3$, ZnO–B_2O_3–SiO_2 did not produce additional phases when sintered with BMT while the others such as SiO_2, B_2O_3–SiO_2, Al_2O_3–SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$, BaO–B_2O_3–SiO_2, MgO–B_2O_3–SiO_2, PbO–B_2O_3–SiO_2 and 2MgO–Al_2O_3–$5SiO_2$ reacted with BMT matrix forming additional phases.
- Certain glasses like B_2O_3, 5ZnO–$2B_2O_3$, ZnO–B_2O_3–SiO_2 enhanced the cation ordering which had fairly good microwave dielectric properties while some other glasses like SiO_2, Al_2O_3–SiO_2, Na_2O–$2B_2O_3 \cdot 10H_2O$ and 2MgO–Al_2O_3–$5SiO_2$ severely destroyed the cation order. This observation emphasized the fact that B-site cation ordering of Mg^{2+} and Ta^{5+} is the fundamental requirement for high quality factor in complex perovskite BMT ceramics. The microwave quality factor is found to be directly related to the order parameter.
- The microwave dielectric properties of pure unannealed BMT ($\varepsilon_r = 24.8$, $\tau_f = 8$ ppm/°C and $Q_u \times f = 80{,}000$ GHz) was improved when it was doped with 1.0 wt% of B_2O_3 ($Q_u \times f = 124{,}700$ GHz, $\varepsilon_r = 24.2$, and $\tau_f = -1.3$ ppm/°C). The unloaded *Q* factor of 0.2 wt% ZnO–B_2O_3-doped BMT is 136,500 GHz while that of 1.0 wt% of 5ZnO–$2B_2O_3$ -added ceramic is $Q_u \times f = 141{,}800$ GHz. The best microwave quality factor is observed for ZnO–B_2O_3–SiO_2 (ZBS) glass-added ceramics which can act as a perfect liquid-phase medium for the sintering of BMT. The microwave dielectric properties of 0.2 wt% ZBS-added BMT dielectric is $Q_u \times f = 152{,}800$ GHz, $\varepsilon_r = 25.5$, and $\tau_f = -1.5$ ppm/°C.

The sintering temperature is brought down to about 1300 from 1650 °C by the addition of a small amount of glass. However, this sintering temperature is much higher than that required for LTCC applications. A possible difficulty in achieving the LTCC temperature may be the presence of the refractory tantalum in the BMT matrix. The results indicate that possibility of lowering the sintering temperature further down for LTCC applications by adding large amounts of glasses. Addition of such glasses not only lowers the sintering temperature but also decreases the dielectric constant and quality factor considerably.

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