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Tailoring the microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics

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Abstract

$Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is a very important microwave dielectric resonator material with a high dielectric constant of about 25, high quality factor and small temperature variation of resonant frequency. The preparation temperature of BMT ceramics is relatively high, about 1650 °C. The microwave quality factor of BMT depends on the ordering of Mg–Ta–Ta ions on the perovskite B-site. In the present paper we report how one can tailor the properties of BMT ceramics by glass addition, slight non-stoichiometry and by dopant addition. (a) It is found that addition of small amount of glasses such as B_2O_3, ZnO–B_2O_3, ZnO–$2B_2O_3$, ZnO–B_2O_3–SiO_2 reduces the sintering temperature, increases density, order parameter and quality factor. (b) Slight Mg or Ba deficiency improves densification, order parameter and quality factor whereas excess Mg or Ba deteriorated the properties (c) Small amounts of dopants such as Sb_2O_5, $MnCO_3$, ZrO_2, WO_3, SnO_2 and ZnO improve the microwave dielectric properties. It is found that the quality factor is maximum when the ionic radii of the dopant ions are close to the weighted average ionic radii of B site ions (i.e. $Mg_{1/3}Ta_{2/3}$), which is 0.653 Å.

Keywords: Sintering; Dielectric properties; Perovskite

1. Introduction

The beginning of this millennium has witnessed a tremendous demand for microwave dielectric resonators in the global market consequent to the growth of telecommunication industry. Due to the incessantly increasing demands for miniaturizing the important passive microwave components such as dielectric resonators and frequency filters, intensive researches have focused on development of loss less dielectric ceramics.[1] In this regard, the complex perovskite ceramics, $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) have attracted much attention because they exhibit excellent dielectric properties at microwave frequencies, such as high dielectric constant (ε_r), high unloaded quality factor (Q_u), and low resonant frequency temperature coefficient (τ_f). Since there are two different B-site cations, there are two different structures that can exist: the disordered (space group $Pm3m$) and the 1:2 ordered states (i.e. –Mg–Ta–Ta–Mg–Ta–Ta–) (space group $P\bar{3}m1$).[2] It was Nomura[3] who made the breakthrough discovery that ordered complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ has high quality factor and temperature stability of the resonant frequency which can be used for microwave dielectric resonator applications. The emergence of $Ba(Mg_{1/3}Ta_{2/3})O_3$ as a high Q dielectric resonator for microwave communication applications has stimulated a new surge of interest among researchers working on the Materials Science aspects of low loss dielectrics.

As dielectric resonators, complex perovskite oxide $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) has shown the ideal dielectric properties in the microwave frequency region and so far no other low loss material could dwarf BMT in this regard. But the sintering temperature of this ceramic is above 1600 °C, which pose practical difficulties since high temperature sintering is not cost effective. The low temperature synthesis of BMT is technologically demanding for application such as Low Temperature Co-fired Ceramics (LTCC) in multilayer devices. The efforts to improve the dielectric properties of these ceramics were carried out by many researchers in resonance with the innovations in the science of advanced material synthesis. The main hurdles in the synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics include (a) the high sintering temperature above 1600 °C where the volatisation of constituent MgO can occur; (b) formation of magnesium free additional phases like $BaTa_2O_6$, $Ba_5Ta_4O_{15}$ and $Ba_4Ta_2O_9$; (c) and thermal destabilization of cation order from 1:2 to 1:1 or disordered perovskite. Alternate synthesizing techniques like solution synthesis have also been attempted[4–6]

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but the dielectric properties are not appreciable for practical applications. Several authors[7,8] used liquid phase sintering as a means for synthesizing $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave dielectric at low temperature with higher density. A number of papers[9] were available in literature dealing with the role of additives on the densification, cation ordering and microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics. The additives such as MnO,[10] SnO_2,[11] NiO,[12] WO_3,[13] ZrO_2,[14] TiO_2,[15] Y_2O_3,[16] V_2O_5,[17] CuO,[18] etc. which when doped to barium magnesium tantalates improved their microwave dielectric properties. But the action of these dopants under different doping conditions of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and the exact role of a dopant in the parent matrix is still regarded as a matter of debate. In addition to that the reason behind the low loss nature of BMT is also an active area of interest, which can throw light into the structure-property relationship of low loss complex perovskite dielectrics.

The above discussion revealed that standardizing the conditions for developing the high Q phase of BMT is of technological as well as academic interest. The present research work took up efforts to improve and tailor the microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ through a series of strategies like (i) glass fluxing, (ii) deliberate introduction of slight cation non-stoichiometry in the BMT crystal lattice and (iii) doping with suitable metal oxides. We investigated the aspect of structure-property relationship of BMT by probing the complex relationship between stoichiometry and dielectric loss of BMT. This has been done by altering the Ba^{2+} and Mg^{2+} cation stoichiometry of ceramic. The low temperature sintering of the ceramic was studied by adding low melting glasses in to BMT precursor. The discovery of ideal wetting glasses, which aid the liquid phase sintering of BMT can be useful for LTCC application of this ceramic. The effect of various dopants on the structure and dielectric properties of BMT was also investigated.

2. Experimental

High purity (>99.9%) powders of $BaCO_3$ (Aldrich Chemicals), $(MgCO_3)_4$ $Mg(OH)_2{\cdot}5H_2O$ (Aldrich Chemicals) and Ta_2O_5 (Nuclear Fuel Complex, Hyderabad) were used as the starting materials for the solid state synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$. The calcination and sintering temperatures were optimized for the highest density and quality factor. The precursor was calcined at 1200 °C for 10 h with intermediate grinding. To study the effect of glass additives, the calcined precursor was then mixed with different weight percentages of the glasses (B_2O_3, $ZnO–B_2O_3$, $5ZnO–2B_2O_3$ and $ZnO–B_2O_3–SiO_2$) and sintered in the temperature range 1300–1500 °C for 4 h. To study the effect of dopants, the precursor was doped with different mol% of additives such as $MnCO_3$, ZnO, ZrO_2, SnO_2, Sb_2O_3 and WO_3 and they are sintered at the optimized temperature of 1625 °C for 4 h. The barium and magnesium non-stoichiometric specimen were sintered at 1600 °C for 4 h while the sintering of undoped stoichiometric BMT was performed at 1650 °C. The phase evolution and crystal structure of the sintered specimen were analyzed using XRD (Philips) and the microstructure was studied using SEM (Jeol, Japan). The polished ceramic pellets with an aspect ratio of two, which is ideal for maximum separation of modes were used for microwave measurements. The dielectric properties of the materials were measured in the microwave frequency range using a network analyzer HP 8510C by standard resonance techniques.[19,20] The TE_{011} mode was used for measuring the dielectric constant, unloaded quality factor (Q_u) and τ_f.

3. Results and discussion

3.1. Effect of glass addition in BMT

A number of strategies have been worked out to reduce the sintering temperature of BMT ceramics, such as (a) chemical synthesis,[21,22] (b) using starting powders with smaller particle size[23] and (c) liquid phase sintering[24] by adding low melting additive into the ceramic. The effect of low melting additives such as NaF, $LiNbO_3$ and $MgO–CaO–Al_2O_3–SiO_2$ (MCAS) have been reported[25–27] in literature in an effort to bring down the sintering temperature, but the $Q_u \times f$ value has been considerably lowered which cannot be afforded in industrial production. In a recent investigation carried out by Surendran et al.,[28] it has been observed that addition of primary glasses like B_2O_3 up to 2 wt.% can bring down the sintering temperature of BMT from 1625 to 1300 °C without appreciable deterioration in the microwave dielectric properties. The addition of 2 wt.% glasses like $ZnO–B_2O_3$, $5ZnO–2B_2O_3$ and $ZnO–B_2O_3–SiO_2$ could bring down the sintering temperature of BMT to 1375, 1330 and 1335, respectively. The addition of glasses like B_2O_3, $ZnO–B_2O_3$, $5ZnO–2B_2O_3$ and $ZnO–B_2O_3–SiO_2$ suppressed the formation of additional phases like $BaTa_2O_6$, $Ba_5Ta_4O_{15}$ and $Ba_4Ta_2O_9$ which could have been detrimental to the properties of BMT dielectric.

The dielectric properties of BMT ceramics fluxed with different amounts of glasses yields interesting results. The microwave dielectric properties of undoped, unannealed $Ba(Mg_{1/3}Ta_{2/3})O_3$ prepared by sintering at 1600 °C 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. In order to promote cation ordering in complex perovskite BMT the sintered samples were subjected to a very slow cooling rate (1°/min). The dielectric constant increased from 24.8 (pure BMT) to 25.02 when the sample was added with 0.2 wt.% of boric oxide and further addition resulted in a decrease of it (see Fig. 1). On adding 0.5 wt.% of $5ZnO–2B_2O_3$ glass, the measured values of ε_r increased to 25.45 and then gradually decreased to 24.5 with 2.0 wt.% of the additive. The maximum value of ε_r for BMT doped with $ZnO–B_2O_3$ were 25.12 for 0.1 wt.% of the additives which decreases on further addition due to the formation of $Zn(BO_2)_2$. For the glass system $ZnO–B_2O_3–SiO_2$ the dielectric constant slightly increases for small values of the glass content and then decreases as the presence of glass in the mixture increases (Fig. 1).

The τ_f of BMT decreases with B_2O_3 and $ZnO–B_2O_3–SiO_2$ addition and approached more negative values when doping level of the glass exceeded. It is interesting to note from Fig. 2 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 τ_f of $ZnO–B_2O_3$ glass doped decreased to −19.8 ppm/°C may be due

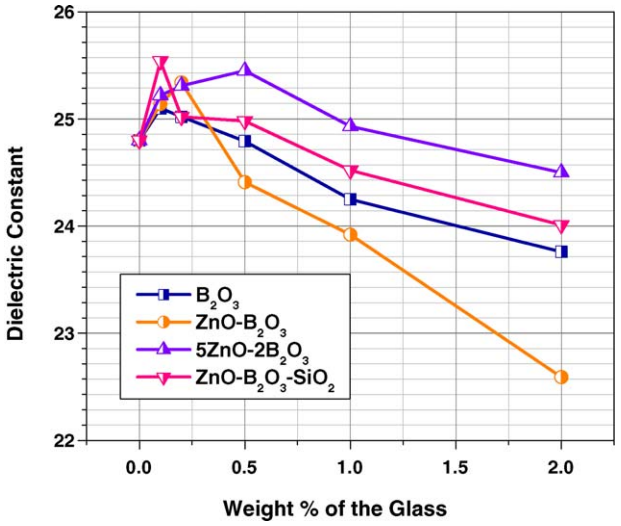

Fig. 1. Variation of dielectric constant of BMT with concentration of the glass additives.

to the formation of $Zn(BO_2)_2$ whose presence has been confirmed through XRD analysis. The temperature coefficient of BMT showed steady values with $5ZnO–2B_2O_3$ glass addition (see Fig. 2).

As shown in Fig. 3, the quality factor of BMT increased for small amount of B_2O_3. For 0.5 wt.% of B_2O_3 addition $Q_u \times f$ reached 124,700 GHz (see Fig. 3). The unloaded quality factor decreased with further addition of B_2O_3 glass where the densification factor also followed a similar trend (see Fig. 1). 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. It is interesting to note that the quality factor of BMT increased steadily with $5ZnO–2B_2O_3$ content. The best microwave property among binary glass added BMT ceramic was found for 1.0 wt.% $5ZnO–2B_2O_3$ where the $Q_u \times f$ was 141,800 GHz. 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 (see Fig. 3). It must be remembered that the reduction in sintering temperature in this research report was not sufficient enough for applications

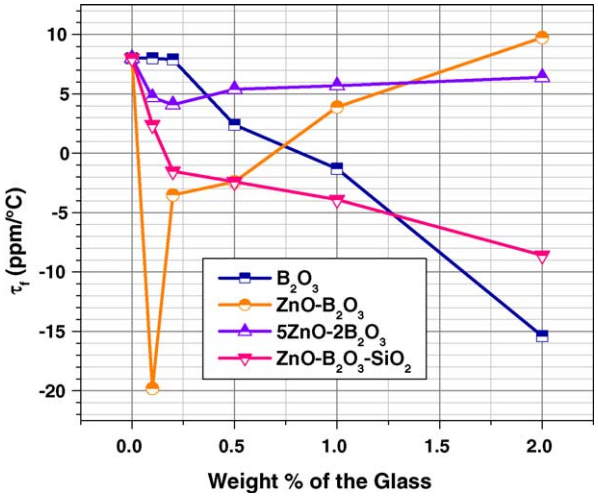

Fig. 2. Variation of τ_f of BMT with concentration of the glass additives.

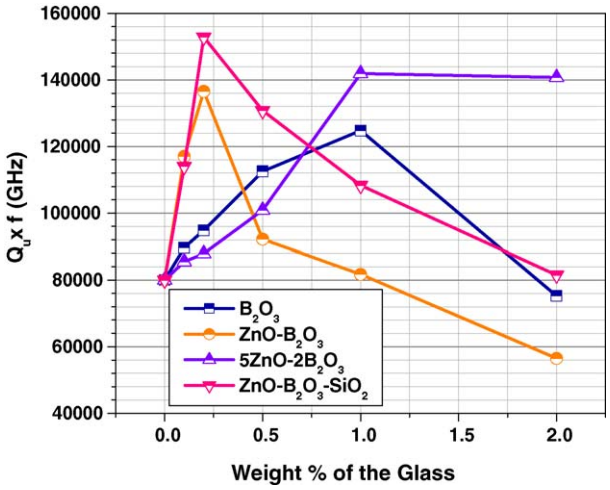

Fig. 3. Variation of quality factor of BMT with concentration of the glass additives.

in multilayer structures using LTCC technique where the sintering temperature must be less than 961 °C which is the melting point of silver electrode.

3.2. Effect of non-stoichiometry in BMT

One method to improve the sinterability of the ceramic is to enhance the material transport processes in the dielectric by altering the material's stoichiometry. Historically, Desu and O'Bryan[29] made the first attempt in correlating the phenomenon of the excellent microwave quality factor of a prominent complex perovskite candidate $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) with *B*-site cation non-stoichiometry. In another significant attempt, Paik et al.[30] investigated the effect of Mg deficiency on the microwave dielectric properties of complex perovskite $Ba(Mg_{0.33}Nb_{0.67})O_3$. It was also reported[31] that among the three starting materials, the reactivity of MgO is inferior to $BaCO_3$ and Ta_2O_5. An improvement in the degree of 1:2 ordering and sinterability was proposed by Lu et al.[32] in Ba-deficient $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics, but they did not study the effects of *A*-site cation deficiency on the microwave dielectric properties of BMT. The effect of Mg deficiency on the microwave dielectric properties of BMT was also investigated by a couple of research groups[33,34] who found that Mg-deficient specimen showed faster rate of grain growth than stoichiometric BMT. However, non-stoichiometric samples showed lower Q values. Recently Surendran et al.[35] revisited the problem of non-stoichiometry in BMT by preparing compositions based on $Ba(Mg_{0.33-x}Ta_{0.67})O_3$ [$x = -0.015, -0.010, -0.005$. 0.0, 0.005, 0.010, 0.015, 0.020, 0.025 and 0.030] and $Ba_{1-x}(Mg_{0.33}Ta_{0.67})O_3$ [$x = -0.015, -0.010, -0.005$. 0.0, 0.0025, 0.005, 0.0075, 0.010, 0.015, 0.020, 0.025 and 0.030]. In this investigation, the effect of Ba and Mg non-stoichiometries on the densification, microstructure, structural ordering and microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ are studied.

Fig. 4 presents the scanning electron micrographs of two non-stoichiometric specimens sintered at 1600 °C. The surface

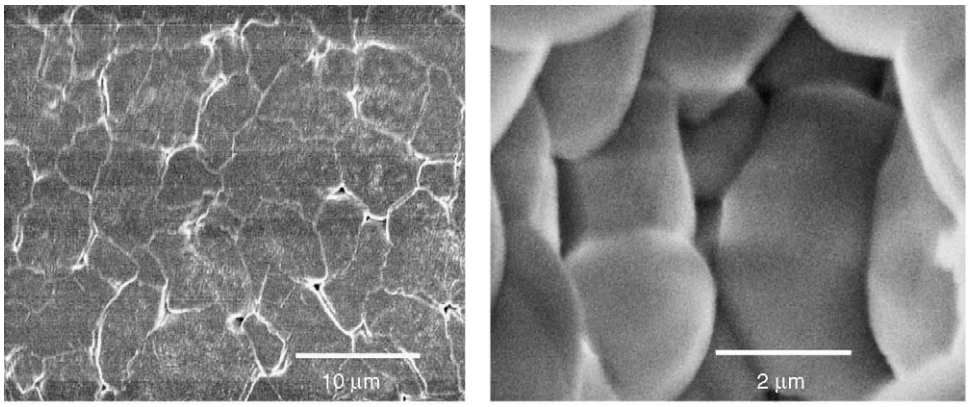

Fig. 4. Scanning electron micrographs of (a) $Ba(Mg_{0.3183}Ta_{0.667})O_3$ and (b) $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$ ceramics.

morphology recorded from a typical Mg deficient BMT ($Ba(Mg_{0.3183}Ta_{0.667})O_3$) sample is given in Fig. 4a. There has been previous reports[37] showing that grain growth will be more rapid in Mg deficient BMT ceramics, consequent to the formation of sandwich type precipitates of $Ba_5Ta_4O_{15}$ within the matrix grain. Here also it is evident that the average size of BMT grain is about 5–8 μm in Mg-deficient specimens, with reasonably good close packing of grains. Fig. 4b represents the surface morphology of $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$ which is taken from a fractured surface. Here, no additional phases are visible in the SEM picture and the grain size is around 2–3 μm. A previous report[32] on the Ba-deficient BMT ceramics observed the presence of magnesium rich small darker grains, which appeared as a solidified liquid. But no evidence of liquid phase sintering was revealed in our Ba-deficient BMT samples.

In the ordered form (space group $P\bar{3}m1$), the Mg^{2+} and Ta^{5+} cations are distributed on individual ⟨1 1 1⟩ planes of the perovskite subcell with alternating {Mg, Ta, Ta} sequence. This results in the appearance of superstructure reflections at [$h \pm 1/3$, $k \pm 1/3$, $l \pm 1/3$] positions. The cation ordering parameter for BMT can be calculated using the following equation

$$S = \sqrt{\frac{(I_{(100)}/I_{(110),(102)})_{\text{observed}}}{(I_{(100)}/I_{(110),(102)})_{\text{theoretical}}}} \quad (1)$$

where the theoretical value of the ratio of the integral intensity of super structural reflection line (1 0 0) to that of (1 1 0, 1 0 2) line, $(I_{100}/I_{110,102})_{\text{theoretical}}$ is 8.3% putting all the atoms in approximate ideal positions in BMT crystal lattice. The recent structural analysis carried out by Janaswamy et al.[36] and Lufaso[37] suggest that a more accurate value for $(I_{100}/I_{110,102})_{\text{theoretical}}$ is equal to 8.7%. This value has been used for the determination of order parameter in this study. The error in the calculation of the ordering parameter was less than ±0.001. The ordering of Mg and Ta ions results in the expansion of the original unit cell along the ⟨1 1 1⟩ direction so that the value of *c/a* assumes a value greater than $\sqrt{(3/2)} = 1.22474$. It is interesting to note that the value of the cell parameter *c* also increases from 7.0699 to 7.0845 Å when *x* changes from 0.0 to 0.015 and the cell parameter ratio *c/a* increases up to $x = 0.015$ (Table 1). On the other hand the lattice parameter ratio is smallest for MgO deficient samples. In Ba-deficient samples the *c/a* ratio increases with *x* and reaches a maximum value for $x = 0.0075$. So it is expected that *B* site cation is fully ordered for the complex perovskite composition $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$. As a general rule, the increase of deviation from the ideal stoichiometry would cause an increase of the volume of the unit cell in complex perovskites.

The splitting of the profiles of (4 2 2) and (2 6 6) reflections due to the lattice distortion of non-stoichiometric $Ba(Mg_{0.33-x}Ta_{0.67})O_3$ and $Ba_{1-x}(Mg_{0.33}Ta_{0.67})O_3$ for different values of *x* are shown in Fig. 5a and b, respectively. The XRD patterns shown in Fig. 5 were recorded with a slow scan of $2\Theta = 1°$/min. At 1600 °C, the temperature is sufficient to attain a highly ordered perovskite, however the sintering time (4 h) is insufficient to reach equilibrium cation order conditions at that temperature. Slow cooling assists in the ordering, but does not guarantee the presence of equilibrium ordering. Changes in composition, which kinetically assists cation ordering are being followed in this experiment. For stoichiometric BMT the profiles of (4 2 2) and (2 6 6) reflections are not distinguishable from standard $K\alpha_2$ line, which has apparently no lattice distortion. It is observed that splitting is more pronounced for $x = 0.015$ in

Table 1
Unit cell parameters of $Ba(Mg_{0.33-x}Ta_{0.67})O_3$ and $Ba_{1-x}(Mg_{0.33}Ta_{0.67})O_3$ for different values of *x*

x	$Ba(Mg_{0.33-x}Ta_{0.67})O_3$			$Ba_{1-x}(Mg_{0.33}Ta_{0.67})O_3$		
	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a
−0.0150	5.7814	7.0678	1.2225	5.7832	7.0711	1.2226
−0.0100	5.7819	7.0680	1.2224	5.7821	7.0709	1.2228
−0.0050	5.7821	7.0671	1.2222	5.7810	7.0714	1.2232
0.0000	5.7720	7.0699	1.2249	5.7720	7.0699	1.2249
0.0025	–	–	–	5.7724	7.0711	1.2249
0.0050	5.7802	7.0799	1.2249	5.7757	7.0800	1.2258
0.0075	–	–	–	5.7749	7.0802	1.2260
0.0100	5.7818	7.0811	1.2247	5.7788	7.0784	1.2248
0.0150	5.7818	7.0845	1.2252	5.7799	7.0780	1.2246
0.0200	5.7820	7.0849	1.2252	5.7805	7.0762	1.2241
0.0250	5.7824	7.0833	1.2249	5.7823	7.0771	1.2233
0.0300	5.7835	7.0821	1.2245	5.7819	7.0691	1.2226

The uncertainties in the determination of lattice parameters are between ±0.0001 and ±0.0003.

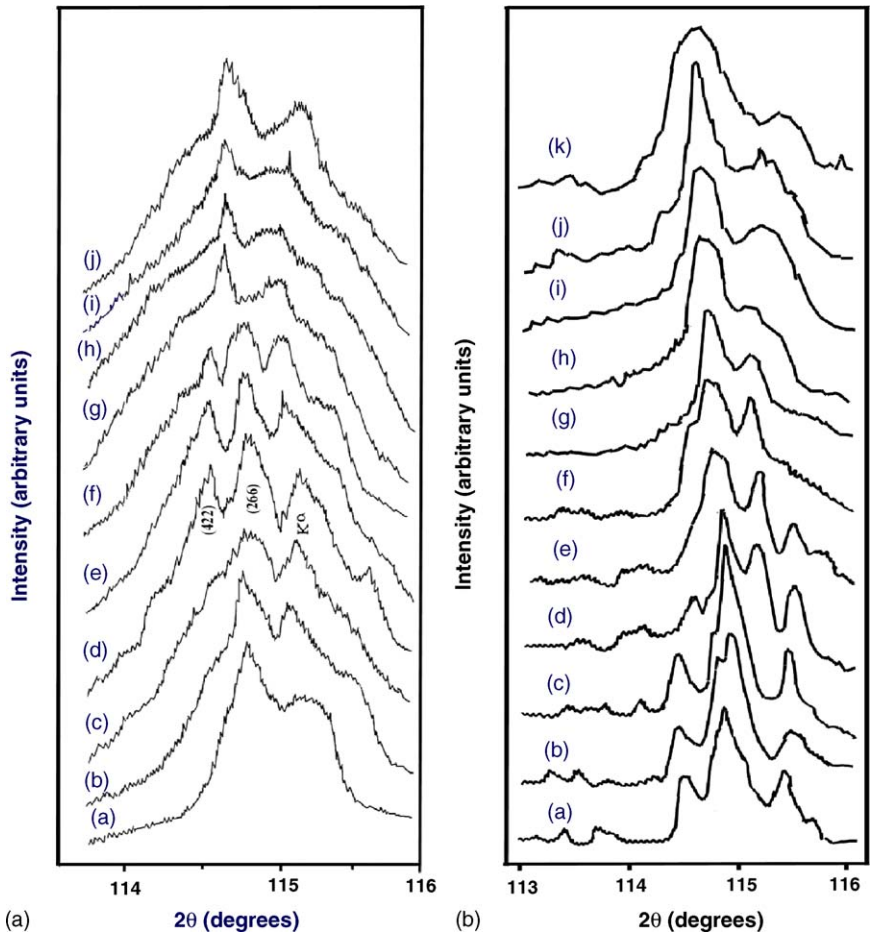

Fig. 5. (a) X-ray diffraction line profiles of (422) and (266) reflections for $Ba(Mg_{0.33-x}Ta_{0.67})O_3$ for x = (a) 0.03, (b) 0.025, (c) 0.02, (d) 0.015, (e) 0.01, (f) 0.005, (g) 0.0, (h) −0.005, (i) −0.010 and (j) −0.015. (b) X-ray diffraction line profiles of (422) and (266) reflections for $Ba_{1-x}(Mg_{0.33}Ta_{0.67})O_3$ for x = (a) 0.0025, (b) 0.005, (c) 0.0075, (d) 0.01, (e) 0.015, (f) 0.02, (g) 0.025, (h) 0.03, (i) −0.005, (j) −0.01 and (k) −0.015.

$Ba(Mg_{0.33-x}Ta_{0.67})O_3$ (see curve *d* in Fig. 5a). A similar phenomenon was observed in Ba-deficient complex perovskites, where the maximum line splitting was observed for $x = 0.0075$ in Ba_{1-x} $(Mg_{0.33}Ta_{0.67})O_3$ (see Fig. 5b). The splitting of the (4 2 2) and (2 6 6) reflections occur at the maximum of the order parameter.

The microwave quality factors of barium and magnesium non-stoichiometric BMT samples are given in Fig. 6. A slight non-stoichiometry may be beneficial for enhanced material transport. The extensive deviation from stoichiometry and the associated point defects in complex perovskite $Ba(Mg_{0.33}Ta_{0.67})O_3$ can give rise to additional losses in BMT. Rong et al.[38] emphasized that the major cause for dielectric loss in complex perovskites is the enhanced concentration of point defects. The $Q_u \times f$ of stoichiometric BMT is 100,500 GHz. For a slight decrease of Mg concentration ($x = 0.015$ in $Ba(Mg_{0.33-x}Ta_{0.67})O_3$) the BMT ceramic observes a marginal increase in quality factor, as $Q_u \times f$ reaches 120,500 GHz. The Mg deficiency and excess Mg may introduce a series of lattice defects in the crystal, apart from the distortion of the octahedral skeleton of oxygen. Consequently, the quality factor decreases. On the other hand, the unloaded quality factor increases with small percentages of Ba deficiency. The quality factor of $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$ is $Q_u \times f = 152{,}580$ GHz. With further increase of x the quality factor decreases. The quality factor of Ba-rich compositions are comparatively lower than Ba deficient samples.

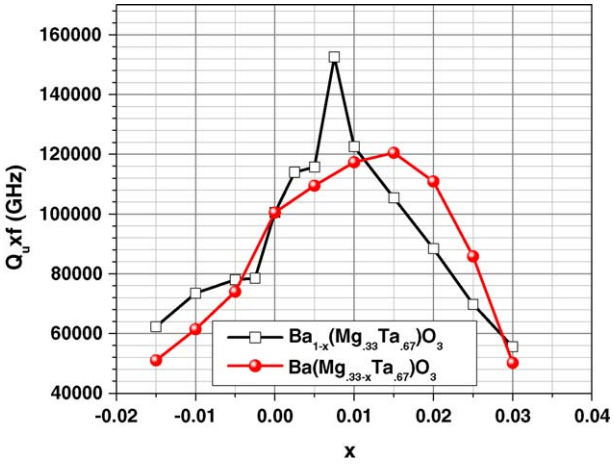

Fig. 6. Variation of unloaded quality factor of $Ba(Mg_{0.33-x}Ta_{0.67})O_3$ and $Ba_{1-x}(Mg_{0.33}T_{0.67})O_3$ as a function of x.

4. Effect of dopants in BMT

The first reported study on the effect of dopants on $Ba(Mg_{1/3}Ta_{2/3})O_3$ was made by Nomura[3] who found that doping with Mn (1 mol%) not only promotes sinterability by lowering the sintering temperature but also increases the unloaded Q value appreciably. A number of parameters starting from the synthesizing stage, up to the final high temperature densification have to be controlled to achieve high Q phase in BMT ceramics.[39] The origin and purity of the initial raw materials also have a considerable influence on the sinterability. Moreover, the particle size of the starting materials, sintering temperature, sintering duration and annealing, etc. make substantial influence on the long range cation ordering and microwave quality factor of BMT[40] when it is prepared through solid state reaction technique.

Recently Surendran et al.[41] made a comprehensive effort on the effect of dopants on the structure and microwave dielectric properties of BMT. The objective of this study was to investigate the effect of various dopants of different ionic radii and valency (such as $MnCO_3$, NiO, ZnO and Co_3O_4, Al_2O_3, Ga_2O_3, Fe_2O_3, In_2O_3, Ce_2O_3, Nd_2O_3 and Bi_2O_3, TiO_2, SnO_2, ZrO_2 and HfO_2, V_2O_5, Sb_2O_3 and Nb_2O_5, WO_3 and MoO_3) on the densification, sinterability, dielectric properties in BMT. Of these additives, $MnCO_3$, ZnO, ZrO_2, SnO_2, Sb_2O_3 and WO_3 when doped to BMT, were observed to have improved dielectric properties. The complex relationship between dielectric loss and the order-disorder transformation on the B-site cations in BMT ceramic materials is also investigated.

The variation of the structural order of BMT, with the concentration dopant is given in Table 2. The order parameter for pure BMT is 0.853, which is increased with dopants except tetravalent ZrO_2. In a significant work Davies[42] proved that the size M^{4+} cation in $(1-x)Ba(Mg_{1/3}Ta_{2/3})O_3$–$xBaM^{4+}O_3$ (cation with an oxidation state 4) plays a critical role in the formation of the 1:1 ordered structure. The introduction of a larger dopant such as Ce (0.87 Å) or Zr (0.72 Å) removes the 1:2 order in BMT and stabilizes a region of 1:1 order that is upto 25 mol% substitution. In our investigation, the ordering parameter of Sn doped ceramic is comparably better (see Table 2) which is thought to be due to 1:2 ordering of the hexagonal perovskite. On the other hand, doping with ZrO_2, decreases the cation ordering. This result substantiates the previous observation[42] which proved that partial substitution with a smaller cation will leave the cation arrangement disordered.

Table 2
B-site cation order parameter of BMT doped with dopants such as $MnCO_3$, ZnO, ZrO_2, SnO_2, Sb_2O_3 and WO_3

Mol% of dopant	$MnCO_3$	ZnO	ZrO_2	SnO_2	Sb_2O_3	WO_3
0.1	0.902	0.833	0.755	0.878	0.881	0.873
0.5	0.895	0.898	0.501	0.825	0.902	0.892
1	0.848	0.794	0.427	0.800	0.894	0.877
2	0.828	0.785	0.105	0.659	0.656	0.578
5	0.705	0.459	–	0.340	0.511	0.265

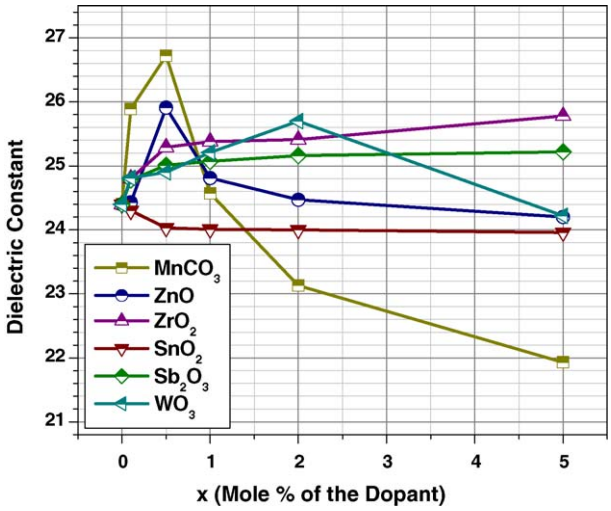

Fig. 7. Variation of the dielectric constant of BMT with concentration of the dopant.

The variation of the dielectric constant of the doped specimen are plotted in Fig. 7. The dielectric constant of Mn and Zn doped samples increase to 26.7 and 25.9 from 24.4 (for pure BMT), respectively, when BMT is doped with 0.5 mol% of the additives. With higher concentration of the dopant ions, the measured dielectric constant decrease which may be due to high temperature phenomena like abnormal grain growth and formation of additional phases.

The temperature coefficient of resonant frequency (τ_f) for pure BMT is 8 ppm/°C as shown in Fig. 8. With exception of SnO_2, the τ_f of most of the doped specimen increases when the dopant level is higher (5 mol%) which is attributed to the possible lattice distortion caused by the partial substitution of the dopant ion at the lattice site of BMT. The effect of SnO_2 on BMT decrease the τ_f to negative values. This observation is consistent with a previous observation by Tien et al.[11] who noted apart from improving its quality factor the τ_f of BMT decreases to negative values on doping with $BaSnO_3$.

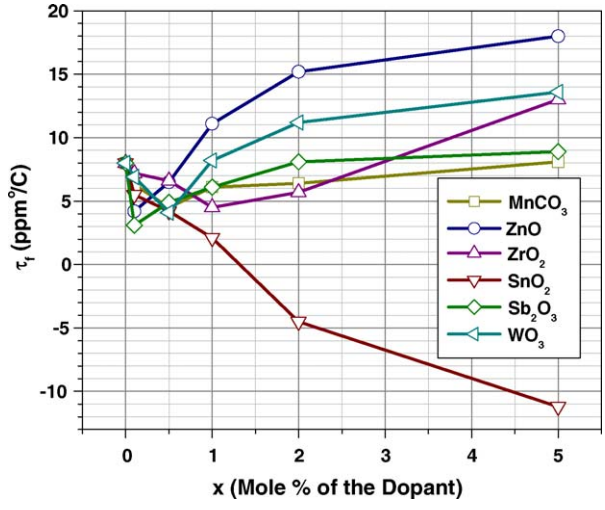

Fig. 8. Variation of the τ_f of BMT with concentration of the dopant.

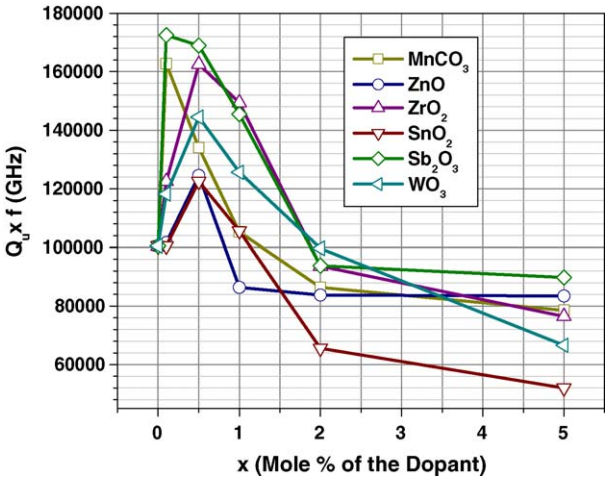

Fig. 9. Variation of the quality factor of BMT with concentration of the dopant.

The microwave dielectric properties of pure as well as doped ones improve with long time annealing. On annealing the BMT samples at 1450 °C for 40 h (which has been the optimized condition for annealing), the dielectric quality factor increases from $Q_u \times f = 80{,}000$–$100{,}500$ GHz. The quality factor of BMT doped with 0.1 mol% of Sb_2O_3 is found to be best ($Q_u \times f = 172{,}500$) among all the additives we studied in this investigation (see Fig. 9). The Mn doped BMT samples are showing high quality factor of $Q_u \times f = 162{,}800$ GHz for 0.1 mol% of the additive which is consistent with the report of Nomura[3]. The quality factor is decreased with further increase of the dopant concentration. When tetravalent additives are added to BMT, the $Q_u \times f$ reaches its maximum value (162,500 GHz) for 0.5 mol% of ZrO_2 dopant where the ordering parameter is 0.501. The ionic radii of W^{6+}, Ta^{5+} and Mg^{2+} with a coordination number 6 are 0.58, 0.64 and 0.72 Å, respectively. A partial substitution of W^{6+} at Ta^{5+} site not only bring about a charge difference of 4 between B′ and B″ site cations, but the ionic radius difference also increases from 0.08 to 0.14 Å. This promotes better cation ordering in the BMT lattice. The quality factor frequency product of 0.5 mol% WO_3 doped BMT is 144,500 GHz which has a comparably good cation ordering (0.892). The ZnO doped

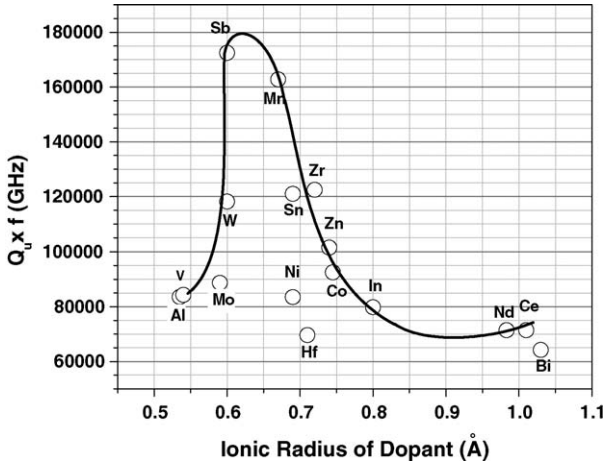

Fig. 10. Plot of ionic radius of the dopant versus quality factor of BMT ceramic.

samples also have a quality factor of $Q_u \times f = 124{,}550$ GHz for 0.5 mol% of the dopant.

A plot of the unloaded quality factor of BMT ceramic doped with 0.1 mol% of the dopants as a function of ionic radius of the dopants is given in Fig. 10. It is clear that when the ionic radius of the dopants are between 0.6 and 0.7 Å (ie close to the average ionic radii of the B-site ion in BMT) the quality factors show maximum values. The average ionic radius of B-site cation of BMT (ie $Mg_{1/3}Ta_{2/3}$) is calculated as 0.653 Å.

5. Conclusions

The sintering temperature of BMT could be reduced to less than 1350 °C with the addition of low melting glasses. 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, $\varepsilon_r = 24.25$, 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) among 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, $\varepsilon_r = 25.54$, and $\tau_f = -1.5$ ppm/°C. Further investigation of these glasses in BMT is needed to bring down its sintering temperature to less than 960 °C which is mandatory for LTCC applications.

The influence of *A* and *B*-site cation non-stoichiometry on the sinterability and microwave dielectric properties of low loss ceramic barium magnesium tantalate is explored by intentionally altering the barium and magnesium ion concentration. The cation ordering between Mg^{2+} and Ta^{5+} ions reaches a maximum for $x = 0.015$ in $Ba(Mg_{0.33}Ta_{0.67})O_3$ which shows better microwave dielectric properties [$\varepsilon_r = 25.1$, $\tau_f = 3.3$ ppm/°C and $Q_u \times f = 120{,}500$ GHz] in Mg deficient specimens. The microwave dielectric properties of $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$ is given by $\varepsilon_r = 24.7$, $\tau_f = 1.2$ ppm/°C, $Q_u \times f = 152{,}580$ GHz. The quality factor of Ba-rich compositions are comparatively lower than Ba deficient samples.

With the addition of dopants the optimized sintering temperature was reduced to 1625 °C. The microwave dielectric properties of pure BMT ceramic sintered at 1625 and annealed at 1450 for 40 h are $\varepsilon_r = 24.4$, $Q_u \times f = 100{,}500$ GHz and $\tau_f = 8$ ppm/°C. With the addition of 0.1 mol% of the divalent impurity $MnCO_3$, the dielectric properties of BMT was increased to $\varepsilon_r = 26.72$, $Q_u \times f = 162{,}800$ GHz, and $\tau_f = 6.3$ ppm/°C. The addition of tetravalent impurities leads to noticeable influence on the cation ordering of BMT ceramics. The cation ordering is poor (0.500) for BMT added with 0.5 mol% of ZrO_2 but the dielectric properties are appreciably higher ($\varepsilon_r = 25.29$, $Q_u \times f = 162{,}500$ GHz, and $\tau_f = 4.5$ ppm/°C). The densification and dielectric properties of BMT is reaching their maximum values with Sb_2O_3 addition. The microwave dielectric properties of BMT when doped with 0.1 mol% of Sb_2O_3 are given as $\varepsilon_r = 24.78$, $Q_u \times f = 172{,}500$ GHz, and $\tau_f = 3.1$ ppm/°C. The addition of hexavalent impurities imparts better ordering in

BMT due to the greater charge difference between B-site cation. The microwave dielectric properties of BMT doped with 0.5 mol% of WO_3 are $\varepsilon_r = 24.9$, $Q_u \times f = 144{,}500$ GHz, and $\tau_f = 4.1$ ppm/°C. The average ionic radius of B-site cation of BMT (i.e. $Mg_{1/3}Ta_{2/3}$) is calculated as 0.653 Å. It is observed that when the ionic radii of the dopants are between 0.6 and 0.7 Å (i.e. close to the average ionic radii of the B-site ion in BMT) the quality factor reaches maximum values.

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