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The effect of dopants on the microwave dielectric properties of $Ba(Mg_{0.33}Ta_{0.67})O_3$ ceramics

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The effect of dopants with different valencies and ionic radii on the densification, structural ordering, and microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is investigated. It is found that dopants such as Sb_2O_5, MnO, ZrO_2, WO_3, and ZnO improve the microwave dielectric properties of BMT. Addition of trivalent dopants is detrimental to the cation ordering and dielectric properties of BMT. A correlation between the microwave dielectric properties of BMT and ionic radii of the dopant has been established. The variation of the dielectric properties of pure and doped BMT at cryogenic temperatures is also discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2127124]

I. INTRODUCTION

Dielectric resonators have achieved an important position, as the key element in microwave filters, antennas, and oscillators. The discovery[1] of the low loss complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) has turned out to be a breakthrough in the research on microwave dielectrics, since it has the highest quality factor reported until date. However, the sintering conditions for obtaining high performance BMT ceramic is very stringent because of its poor sinterability (sintering temperature is higher than 1600 °C), which is thought to be due to the formation of some satellite secondary phases in the calcined powders. Solution chemistry offers alternative approaches such as sol-gel technique for synthesis of BMT powders.[2] But the chemical synthesis of BMT was not the most appropriate method for industrial production due to the complexity of the procedures involved, high cost of production, and comparatively poor microwave dielectric properties.[2]

In a significant study, Nomura[3] found that doping of BMT with 1 mol % of Mn not only promotes sinterability by lowering the sintering temperature but also increases the unloaded Q value appreciably. Later on Matsumoto *et al.*[4] studied doping effects of SnO_2 in BMT, which too yielded excellent microwave dielectric properties. Their study revealed that on addition of 10–15 mol % of $BaSnO_3$ into BMT ceramics increased the Q value up to 33 000 at 10 GHz and the τ_f approached negative values. In another report[5] Yoon *et al.* added hexavalent WO_3 in the form of $BaWO_4$ and found that the addition of barium tungstate up to 5 mol % increased the lattice constant ratio (c/a), order parameter, density, and dielectric quality factor due to the substitution of Ta^{5+} by W^{6+} at above 1430 °C. The effect of nickel on the microwave dielectric properties of BMT has also been studied.[6] It was found that the dielectric properties such as ε_r and τ_f were slightly increased with the substitution of Ni^{2+} ion at Mg^{2+} site in $Ba(Mg_{1/3}Ta_{2/3})O_3$, but the quality factor was decreased. The effects of low melting additives[7] such as NaF reduced the processing temperature of BMT but the formation of secondary phases such as Na_3TaO_4 should be suppressed to achieve stable high Q phase. Chai *et al.*[8] and Chai and Davies[9] reported that with the addition of tetravalent ions, the 1:2 ordering of B-site cations in complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics was transformed into 1:1 ordering with partial substitution of Zr^{4+}, Ce^{4+}, and Sn^{4+} to the $(Mg_{1/3}Ta_{2/3})^{4+}$ site. However, the above report provided no information as to how the microwave dielectric properties of BMT vary with B-site substitution. Shirey[10] reported that the quality factor deteriorated with Ga addition in BMT, nevertheless a reduction in sintering temperature. The densification and quality factor of low loss BMT were also reported[11] to be improved with the addition of Y_2O_3. Another recent study[12] suggested that the addition of pentavalent dopant such as V_2O_5 did not significantly affect the temperature coefficient of resonant frequency but it improved the microwave quality factor consequent to the substitution of V^{5+} in the Ta^{5+} site. Recently Surendran *et al.*[13] reported that the addition of suitable glasses reduce the sintering temperature and improve the quality factor of BMT. It has also been reported[14] that a slight nonstoichiometry of Mg or Ba can improve the density, order parameter, and thereby the quality factor.

Hence from a brief literature survey made above, it is clear that even though BMT ceramic possess the highest Q factor in literature, a comprehensive effort is needed to correlate the complex relationship between the structure and low loss nature of BMT. A number of parameters starting from the synthesizing stage, up to the final high-temperature

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densification have to be controlled to achieve high Q phase in BMT ceramics.[15] The origin and purity of the initial raw materials also have a considerable influence on the sinterability. Though many research groups have studied the effect of various additives on the microwave dielectric properties and sinterability of BMT, the doping was performed under different conditions: sometimes before calcination and sometimes after. Hence the reported Q values show a wide scatter, which may be due to the different measuring techniques used and variations in the synthesizing conditions. To overcome this difficulty, we carried out a comprehensive investigation in which aliovalent and isovalent additives were added to the calcined BMT under similar conditions in a systematic way. The aim of this study was to investigate the effect of various dopants of different ionic radii and valency on the densification, sinterability, and dielectric properties of BMT. The complex relationship between dielectric loss and the order-disorder transformation on the B-site cations in BMT ceramic materials is also presented in this paper.

II. EXPERIMENT

A. Synthesis

The $Ba(Mg_{1/3}Ta_{2/3})O_3$ precursor was prepared by the conventional solid-state ceramic technique. High-purity (>99.9%) powders of $BaCO_3$ (Aldrich Chemicals), $(MgCO_3)_4Mg(OH)_2 \cdot 5H_2O$ (Aldrich Chemicals), and Ta_2O_5 (Nuclear Fuel Complex, Hyderabad) were used as the starting materials. The chemicals were weighed according to the stoichiometric compositions and were ball milled in deionized water for 24 h. The slurry was dried in an oven at 100 °C and calcined in a platinum crucible at 1200 °C for 10 h with intermediate grinding. The calcined BMT precursor was divided into several batches and different mol % of divalent (MnO, NiO, ZnO, and Co_3O_4), trivalent (Al_2O_3, Ga_2O_3, Fe_2O_3, In_2O_3, Nd_2O_3, and Bi_2O_3), tetravalent (TiO_2, SnO_2, ZrO_2, $CeO_{2-\delta}$, and HfO_2), pentavalent (V_2O_5, Sb_2O_3, and Nb_2O_5), and hexavalent (WO_3 and MoO_3) dopants were added to the calcined BMT. The calcined powder was then ground thoroughly for several hours and 3 wt % aqueous solution of polyvinyl alcohol (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 a tungsten carbide die. 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 at 1625 °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/h. The well-sintered samples were annealed at 1450 °C for 40 h to relieve the lattice strain and to enhance cation ordering mechanism. 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.

B. Characterization

The bulk density of the sintered samples were measured using Archimedes method. The powdered samples were used for analyzing the x-ray diffraction patterns using Cu $K\alpha$ radiation (Philips x-ray diffractometer). The cell parameters reported in this paper have been derived from powder-diffraction data of all the diffraction lines in the range $2\theta = 5° - 70°$ and then taking the weighted average. The possible error in the measurement of lattice parameters is in the range of ±0.000 05 which was calculated using the method of least squares. The cation order parameter for BMT was 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 (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. In real case where the structure factors of major reflections (which is a function of ions located in crystal structure) can vary slightly with dopant substitutions. The recent structural analysis carried out by Janaswamy *et al.*[16] and Lufaso[17] suggest that a more accurate value for $(I_{100}/I_{110,102})_{\text{theoretical}}$ is equal to 8.7%. This value has been used in the present calculation. The error in the calculation of the order parameter was less than ±0.001.

The dielectric properties of the materials were measured in the microwave frequency range using a fully automated vector network analyzer HP 8510C (Hewlett-Packard, Palo Alto, CA). The dielectric constant ε_r was measured by Hakki and Coleman[18] method 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.[19] The accuracy of ε_r measurement is restricted to the accuracy in measurement of resonant frequency and dimensions of the sample. The error in ε_r measurement was typically less than ±0.01. Usually, three samples were prepared in a batch and the measurements were made at least twice per each specimen. 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. The coefficient of thermal variation of resonant frequency (τ_f) was measured by noting the temperature variation of the resonant frequency of TE_{011} mode in the reflection configuration over a range of temperature 20–80 °C when the sample was kept in the end shorted position.

The measurement system used for microwave characterization of the samples at cryogenic temperature consists of network analyzer (HP 8722 C), closed cycle refrigerator (APD DE-204), temperature controller (LTC-10), vacuum dewar, a personal computer, and a $TE_{01\delta}$ mode post dielectric resonator. The resonator loaded with the sample was cooled from room temperature to approximately 17 K. Using the network analyzer the $TE_{01\delta}$ mode is identified. The S_{21}, S_{11}, and S_{22} parameter data sets around the resonance were measured at a temperature of 17 K. The transmission mode Q-factor (TMQF) technique[20] has been used to process the data and to estimate the coupling coefficients (k_1 and k_2) and the unloaded Q factor. For higher temperatures only S_{21} was

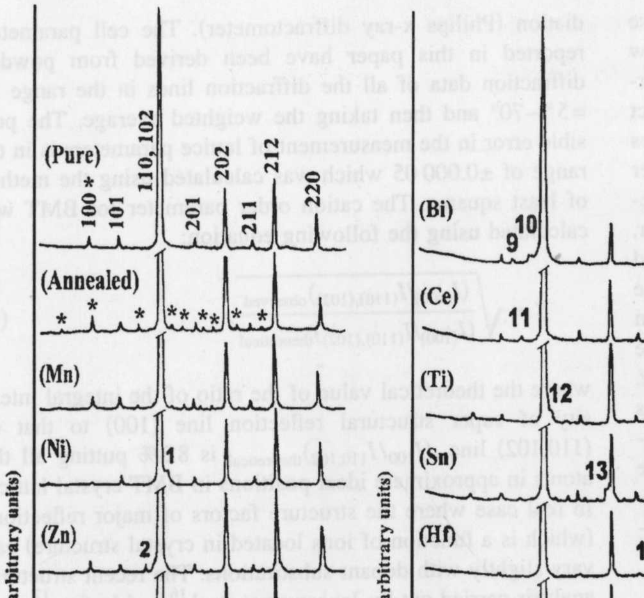

FIG. 1. Powder-diffraction pattern of BMT doped with 5 mol % of the additives. (*) superstructural reflections, (Pure) BMT undoped and (unannealed). (Anneled) BMT undoped and annealed at 1450/40h, (1) $Ba_3NiTa_2O_9$, (2) $Ba_4Ta_2O_9$, (3) $BaCoO_{2.93}$, (4) $Ba_{10}Al_2O_{13}$, (5) $BaGa_{12}O_{19}$, (6) $Fe_4Ta_2O_9$, (7) $InTaO_4$, (8) Nd_2O_3, (9) Bi_2O_3, (10) $BaBiO_3$, (11) $BaCeO_3$, (12) $BaTiO_3$, (13) $BaSnO_3$, (14) Ba_2HfO_4, (15) $BaZrO_3$, (16) BaV_3O_8, (17) $VTaO_4$, (18) $BaWO_4$, and (19) $BaMoO_4$.

measured and the unloaded Q factor was calculated using a simplified TMQF method.[21] The simplified TMQF method calculates the coupling coefficient of both ports at each measurement temperature and hence the accurate unloaded Q factor. The perpendicular component of the real part of relative permittivity and loss tangent is calculated from the resonant frequency and unloaded Q factor, respectively.

III. RESULTS AND DISCUSSION

A. XRD analysis

The dopants used in this investigation are classified as a function of their stable oxidation states as divalent, trivalent, tetravalent, pentavalent, and hexavalent. Aliovalency and comparable ionic size with B-site cations are taken as the basic criterion for selecting dopants in this study. The x-ray diffraction (XRD) patterns of an unannealed pure ceramic sintered at 1625 °C and a sample annealed at 1450 °C for 40 h are given in Fig. 1. The superstructure reflections are clearly seen in the powder-diffraction pattern recorded from the annealed specimen. This observation is attributed to the existence of small 1:2 ordering domains, which grow at higher temperatures on annealing. The XRD patterns of BMT doped with 5 mol % of different dopants are also given in Fig. 1. When an additive is added to BMT, the following phenomena are possible to happen: (a) the dopant ion may partially substitute for A or B site in BMT, (b) the additive melts and may aid in liquid phase sintering, and (c) the additive reacts with the matrix and forms secondary phase with it. Owing to the limitations of XRD as a comprehensive tool for structural analysis, the possibility of trivalent ion substituting at any of the B site in BMT could not be explored, but it is reasonable to expect that bigger trivalent dopant ions such as Nd and Bi can go into the A site to form a structure $Ba_{1-3x}(Nd/Bi)_{2x}(Mg_{1/3}Ta_{2/3})O_3$. Of the trivalent additives we have used in this investigation, the only additives which

TABLE I. Unit-cell properties and densification of pure and doped BMT. The standard deviation in the determination of lattice parameters *a* and *c* are ±0.00005.

BMT + dopant	Mol % of dopant	c/a	Cell volume (Å)^3	X-ray density (g/cm^3)	Percentage densification	Order parameter
Pure	0	1.2243	205.499	7.625	93.0	0.818
MnO	0.1	1.2251	205.213	7.636	95.9	0.902
NiO	0.1	1.2243	205.526	7.624	95.6	0.833
ZnO	0.5	1.2248	205.556	7.623	97.1	0.898
Co_3O_4	1.0	1.2239	205.606	7.621	94.1	0.459
Al_2O_3	0.1	1.2248	205.068	7.641	93.3	0.686
Ga_2O_3	0.1	1.2244	205.531	7.624	93.5	0.889
Fe_2O_3	0.1	1.2246	205.004	7.643	95.5	0.795
In_2O_3	0.1	1.2244	205.530	7.624	95.3	0.615
Nd_2O_3	0.1	1.2233	205.336	7.631	95.1	0.86
Bi_2O_3	0.1	1.2237	205.082	7.640	98.1	0.647
TiO_2	0.1	1.2244	205.579	7.622	97.6	0.386
SnO_2	0.5	1.2247	205.161	7.638	97.9	0.825
HfO_2	0.1	1.2227	205.449	7.627	98.3	0.467
ZrO_2	0.5	1.2240	206.229	7.598	97.1	0.500
$CeO_{2-\delta}$	0.5	1.2234	204.949	7.645	94.1	0.825
V_2O_5	0.1	1.2238	205.021	7.642	93.4	0.730
Sb_2O_3	0.1	1.2252	204.833	7.650	95.1	0.881
Nb_2O_5	0.1	1.2233	205.336	7.631	94.2	0.759
WO_3	0.5	1.2249	204.949	7.646	96.7	0.892
MoO_3	0.5	1.2232	205.367	7.630	97.5	0.462

have the ionic radii close to 1 Å are Nd^{3+} (0.983 Å) (Ref. 23) and Bi_2O_3 (1.03 Å) which are likely to substitute the Ba site in $Ba(Mg_{1/3}Ta_{2/3})O_3$. In a previous report,[22] a bigger trivalent ion such as La^{3+} doped in BMT results in the formation of a 1:1 ordered structure coexisting with 1:2 ordered phase. It is evident that the addition of trivalent Bi_2O_3 severely damages the cation ordering arrangement of BMT on higher concentration of the dopant as there are hardly any superstructure reflections in the XRD pattern [Fig. 1 (Bi)].

The XRD pattern of BMT doped with 5 mol % of Sb_2O_3 is given in Fig. 1 (Sb). It is well known that at high temperatures, the oxidation state of Sb will change to 5, which may partially replace the Ta site in BMT. Here the XRD pattern is well ordered and no trace of any additional peak is visible in the XRD spectrum, which is reflected in the excellent microwave dielectric properties of BMT ceramics doped with Sb_2O_3. In the case of Sb_2O_3 doping, the size difference[23] between partially substituted Sb^{5+} ion (0.6 Å) in the Ta^{5+} site with Mg^{2+} ion (0.72 Å) is 0.12 which effectively promotes the cation ordering. The doping with Nb_2O_5 also does not form any secondary phase with BMT [Fig. 1 (Nb)] which is understood since Nb^{5+} has an ionic radius same as that of Ta^{5+} (0.64 Å).[23] Kim *et al.*[24] found that WO_3 doping enhances the 1:2 ordering of BMT due to the greater difference in charge and ionic radius between W^{6+} and Ta^{5+} ions when the latter substitutes at the Ta site. In the present study it was revealed that the influence of hexavalent dopants enhanced the *B*-site cation ordering in complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ due to obvious reasons of increased charge difference between the additive cation and divalent Mg in the *B'*-site of BMT.

B. Densification

The percentage densification and unit-cell properties of doped BMT which corresponds to the best of their microwave dielectric properties for each dopant are given in Table I. The densification is comparatively larger for ZnO. But the addition of dopants in large amount have a detrimental effect on densification as it may breed grain growth. The densification is very poor for Al_2O_3 doped samples, which is attributed to the formation of barium aluminate [see Fig. 1 (Al)]. Apart from Nd^{3+} and Bi^{3+} ions, all other dopants in this family probably may substitute only at the *B* site of the complex perovskite. It is interesting to note from Table I that the densification behavior of Bi_2O_3 dopant in BMT is best among the trivalent dopants we used in this study, which is believed to be due to liquid phase sintering. Nevertheless, it could not lead to any improvement in the dielectric properties of BMT ceramics as shown later. With exception of $CeO_{2-\delta}$, the tetravalent additives perform fairly well (>97% of their theoretical density) in densifying the BMT (see Table I). On addition of more than 0.5 mol % of the dopant, the density decreases, due to obvious reasons of formation of secondary phase $BaMO_3$ (M=Ti, Sn, Zr, Ce, and Hf) as evidenced by the XRD analysis given in Fig. 1. The densification behavior of Sb_2O_3 is good among pentavalent additives, whose cation is likely to replace Ta^{5+} in BMT. On the other hand, the doping with V_2O_5 does not improve the density as it resulted in the formation of secondary phases such as BaV_3O_8 and $VTaO_4$ [see Fig. 1 (V)]. This result is contradictory to a recent observation made by Huang *et al.*[12] who observed an increase in the density and dielectric properties of BMT with V_2O_5 addition for obvious reasons of liquid phase sintering and partial substitution of V^{5+} at the Ta^{5+} site. There is a marginal improvement in density for BMT doped with small amount of WO_3 and MoO_3.

C. Cation ordering

The properties of the unit cell of undoped and doped BMT are given in Table I. The present investigation revealed that for pure ordered complex perovskite BMT sintered at 1625 °C assuming a trigonal superstructure, the unit-cell parameters are $a=5.7807(2)$ Å and $c=7.0840(1)$ Å. The x-ray density of pure BMT=7.625 g/cm^3, assuming the molecular weight to be 314.596 g.[25] In the ordered state, the unit cell of BMT expands along the $\langle 111 \rangle$ direction so that $c/a \geq \sqrt{(3/2)}=1.2247$. When sintered BMT samples are annealed at 1450 °C for 40 h, the modified cell parameters are $a=5.7878(1)$ Å and $c=7.0930(4)$ Å so that $c/a=1.2255$. The order parameters of pure unannealed and annealed BMT are 0.755 and 0.818, respectively.

It is well known that the presence of dopants lead to changes in lattice parameters if they go into the lattice site of the matrix. The unit-cell parameters a and c are modified slightly by doping with divalent ion as seen from Table I. A partial substitution of Mg^{2+} with Mn^{2+} enhances the cation ordering in BMT which is confirmed by the increase in the values of order parameter. Addition of NiO has been detrimental to its cation ordering and dielectric properties due to the formation of secondary phase $Ba_3Ni_3O_6$.[26] It must be noted that among all the trivalent dopants we studied in this work, not even a single dopant improved the 1:2 cation arrangement in BMT so that c/a is greater than 1.2247 (see Table I). This observation categorically points out that the trivalent additives are unsuitable for improving the properties of BMT ceramics. The formation of secondary phases may be probably the reason behind the poor ordering of B-site cations in BMT doped with trivalent ions. The cation order parameter of Sn doped ceramic is reasonably good (see Table I) which is due to 1:2 ordering of the trigonal perovskite. In a previous report, Davies[27] found that introduction of a larger dopant such as Ce (0.87 Å) or Zr (0.72 Å) destroys the 1:2 order in BMT and stabilizes a region of 1:1 order when the substitution levels are up to 25 mol %. But in the present study, no 1:1 ordering powder-diffraction peaks are observed since the maximum dopimg level is only up to 5 mol %. The order parameter of BMT doped with TiO_2 is poor which is reflected in the dielectric properties of these ceramic at microwave frequencies. This may be due to the presence of secondary phase of $BaTiO_3$ which is a lossy material with high dielectric constant. The cation ordering is only 0.5 when the concentration of the ZrO_2 dopant is 0.5 mol %. On the other hand the cation ordering is poor in HfO_2 doped BMT. It is evident that the doping of Sb_2O_3 is found to be excellent among the 20 dopants we used in this investigation in terms of the dielectric properties in the microwave frequency region. The doping of V_2O_5 and Nb_2O_5 did not produce any significant contribution towards the ordering. The cation ordering is higher for WO_3 than MoO_3 additions, (see Table I) which could be due to the partial substitution of W at the Ta site in BMT.

D. Microwave dielectric properties

1. Divalent dopants

The microwave dielectric properties of pure BMT ceramic samples sintered at 1625 °C for 4 h before annealing are $\varepsilon_r=24.3$, $Q_u x f=80\,000$ GHz, and $\tau_f=7$ ppm/°C. On annealing the samples at 1450 °C for 40 h (which has been the optimized condition for annealing), the dielectric properties are $\varepsilon_r=24.4$, $Q_u x f=100\,500$ GHz, and $\tau_f=8$ ppm/°C. Figure 2(a) shows microwave dielectric properties of BMT ceramics doped with divalent dopants such as MnO, NiO, ZnO, and Co_3O_4. The dielectric constant of 0.5 mol % Mn^{2+} and Zn^{2+} doped BMT samples increase to 26.7 and 25.9, respectively, due to the higher ionic polarizabilities of Mn and Zn ions (2.64 and 2.04, respectively). With higher concentration of the dopant ions, the measured dielectric constant decreases. For Ni and Co additives, the dielectric constant decreases with larger amount of doping which is consistent with previous reports.[28] The temperature coefficient of resonant frequency (τ_f) increases with doping for NiO, Co_3O_4, and ZnO additives while τ_f decreases for MnO addition. The Mn doped BMT samples are showing high quality factor of $Q_u x f=162\,800$ 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. The ZnO doped samples (0.5 mol %) also have reasonably good quality factors ($Q_u x f=124\,550$ GHz). Among the divalent dopants we studied, the lowest quality factor is found for NiO doped samples as seen from Fig. 2(a).

2. Trivalent dopants

The microwave dielectric properties of BMT dielectrics doped with dopants with oxidation state of 3 are found to be comparatively poor as shown in Fig. 2(b). This is attributed to the formation of lossy secondary phases. The dielectric constant of Bi and Nd doped ceramics show higher values, which can be attributed to the high dielectric polarizabilities (6.12 and 6.15, respectively) of these cations. It is worthwhile to note that if the trivalent dopant's ionic polarizability is lower than the average polarizability (=3.693) (Ref. 29) of the B-site cation in BMT, then the measured dielectric constant decreases. The temperature coefficient of resonant frequencies of BMT as a function of trivalent dopant is given in Fig. 2(b). Except for Al_2O_3 and Ga_2O_3, the doped samples show high positive τ_f values. In Ga and Al doping, τ_f approaches negative values, which can be due to the formation of secondary phase such as $BaGa_{12}O_{19}$ and $Ba_{10}Al_2O_{13}$, respectively. For other dopants such as Fe_2O_3, Al_2O_3, In_2O_3, and Nd_2O_3, high positive values of τ_f are observed. In general, the quality factor is poor for BMT doped with trivalent additives.

3. Tetravalent dopants

The dielectric properties of tetravalent dopant added BMT measured at microwave frequency are plotted in Fig. 2(c). The ε_r of all doped BMT samples are increased as compared for pure BMT, except for SnO_2 addition. Though the dielectric polarizability[29] of Zr (3.25) is more than that of Ti (2.93), the dielectric constant of samples doped with

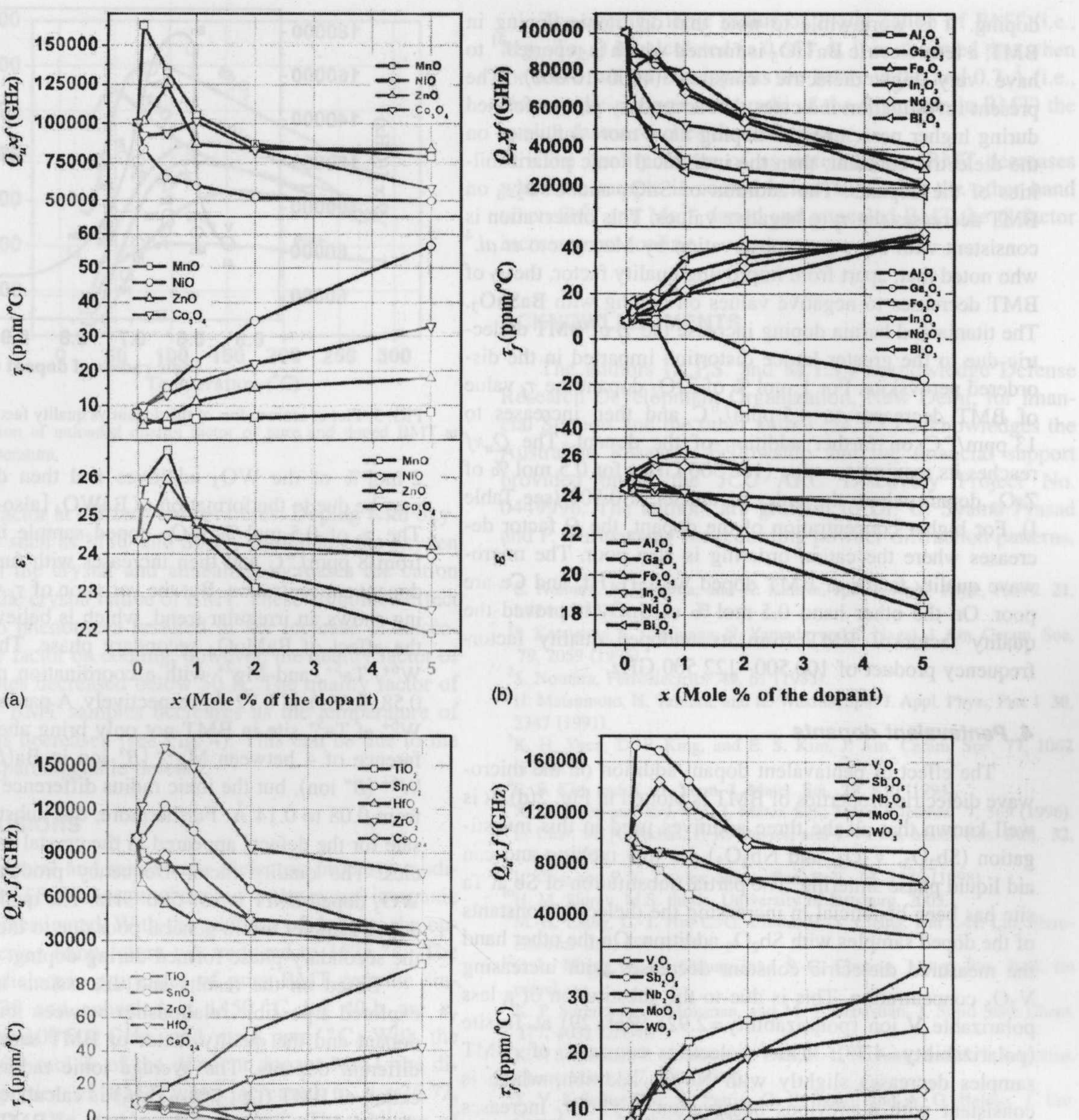

FIG. 2. (a) Variation of dielectric properties of BMT with the addition of divalent dopant. (b) Variation of the microwave dielectric properties of BMT with trivalent dopant addition. (c) Variation of the microwave dielectric properties of BMT with the addition of tetravalent dopant. (d) Variation of the microwave dielectric properties of BMT with the addition of pentavalent dopant. (e) Variation of the microwave dielectric properties of BMT with the addition of pentavalent and hexavalent dopants.

5 mol % TiO_2 has higher values (ε_r=27.5) than that doped with an identical concentration of ZrO_2 (25.8). The increase in dielectric constant is believed to be of lattice distortion of the perovskite structure due to the substitution of tetravalent cation dopant. In a previous report, Lan *et al.*[30] also observed a small enhancement of dielectric constant of BMT with Zr

doping. It is worthwhile to note that on titania doping in BMT, a ferroelectric $BaTiO_3$ is formed which is reported[31] to have very high dielectric constant (4000–10 000). The present investigation indicates that secondary phases formed during higher percentage of doping have more influence on the dielectric constant, than the individual ionic polarizabilities of the dopants. The addition of SnO_2 and $CeO_{2-\delta}$ on BMT decreases the τ_f to negative values. This observation is consistent with a previous observation by Matsumoto *et al.*[4] who noted that, apart from improving quality factor, the τ_f of BMT decreases to negative values on doping with $BaSnO_3$. The titania and hafnia doping increase the τ_f of BMT dielectric due to the greater lattice distortion imparted in the disordered perovskite. For 1 mol % of ZrO_2 dopant the τ_f value of BMT decreases to 4.5 ppm/ °C and then increases to 13 ppm/ °C on further addition of the dopant. The $Q_u xf$ reaches its maximum value (162 500 GHz) for 0.5 mol % of ZrO_2 dopant where the order parameter is 0.500 (see Table I). For higher concentration of the dopant, the Q factor decreases where the cation ordering is also poor. The microwave quality factor of BMT doped with Ti, Hf, and Ce are poor. On the other hand 0.5 mol % of SnO_2 improved the quality factor of BMT from its undoped quality factor-frequency product of 100 500–122 500 GHz.

4. Pentavalent dopants

The effect of pentavalent dopant addition on the microwave dielectric properties of BMT is plotted in Fig. 2(d). It is well known that all the three additives used in this investigation (Sb_2O_3, V_2O_5, and Nb_2O_5) are low melting and can aid liquid phase sintering. The partial substitution of Sb at Ta site has been beneficial in increasing the dielectric constants of the doped samples with Sb_2O_3 addition. On the other hand the measured dielectric constant decreases with increasing V_2O_5 concentration. This is due to the substitution of a less polarizable V ion (polarizability=2.92) (Ref. 29) at Ta site (polarizability=4.73). The dielectric constant of BMT samples decreases slightly with Nb_2O_5 addition, which is consistent with a previous observation.[32] The τ_f increases monotonously with increase in the V_2O_5 and Nb_2O_5 content. The τ_f values are 3.1 and 4.9 ppm/ °C when BMT is doped with 0.1 and 0.5 mol % of Sb_2O_3 additive. The quality factor of BMT doped with 0.1 mol % of Sb_2O_3 is found to be the best ($Q_u xf$=172 500 GHz) among all the dopants we studied. It is worthwhile to note that the cation ordering is larger for samples doped with Sb_2O_3. For other dopants V_2O_5 and Nb_2O_5, the loss factor increases with dopant concentration. The lowering of Q with V_2O_5 addition disagrees with a recent observation by Huang *et al.*[12] who observed an enhancement of the quality factor with V_2O_5 incorporation due to the liquid phase sintering.

5. Hexavalent dopants

The microwave dielectric properties of the BMT ceramics doped with MoO_3 and WO_3 are also given in Fig. 2(d). For 0.1 mol % of MoO_3 additive the ε_r increases from 24.4 to 25.17 and then decreases on further addition. On the other hand the dielectric constant steadily increases to 25.7 up to 2 mol % of the WO_3 additives and then decreases which may be due to the formation of $BaWO_4$ [also see Fig. 1 (W)]. The τ_f of 0.5 mol % WO_3 doped sample improved to 4.1 from 8 ppm/ °C and then increases with further increase in dopant concentration. But the variation of τ_f with MoO_3 doping shows an irregular trend, which is believed to be due to the effect of $BaMoO_4$ secondary phase. The ionic radii of W^{6+}, Ta^{5+}, and Mg^{2+} with a coordination number of 6 are 0.58, 0.64, and 0.72 Å, respectively. A partial substitution of W^{6+} at Ta^{5+} site in BMT not only bring about a charge difference of 4 between Mg^{2+} [B' ion in $Ba(B'_{1/3}B''_{2/3})O_3$] and W^{6+} (B'' ion), but the ionic radius difference[23] also increases from 0.08 to 0.14 Å. Furthermore, this substitution compensate for the defects appeared in the crystal as O^{2-} ion vacancies. The quality factor frequency product of 0.5 mol % WO_3 doped BMT is 144 500 GHz. The quality factor MoO_3 doped samples are in general poor due to the lossy effects of the secondary phase formed during doping.

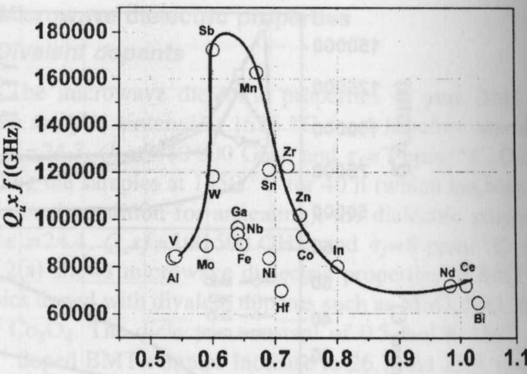

FIG. 3. Plot of ionic radius of the dopant vs quality factor of BMT ceramic.

Based on the results and discussions made above, we explored a possible relationship between ionic radius of the dopant and the quality factor of BMT samples added with different dopants. The average ionic radius (IR) of *B*-site cation of BMT (i.e., $Mg_{1/3}Ta_{2/3}$) is calculated as 0.653 Å. 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. 3. In general 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. However, cations such as Ga (IR=0.64 Å), Nb (IR=0.64 Å), and Fe (IR=0.645 Å) (Ref. 23) are not favorable for improving the properties of BMT.

6. Dielectric properties at cryogenic temperatures

Figure 4 represents the variation of quality factor of pure and doped and annealed BMT in the temperature range of 19 to 292 K. The undoped BMT used in this study was not annealed. Here the dielectric loss of unannealed BMT increases with the decrease of temperature due to the presence of paramagnetic defects.[33] In addition to this, it is possible that unannealed BMT may contain considerable amount of point defects such as oxygen vacancies[34] which also decrease

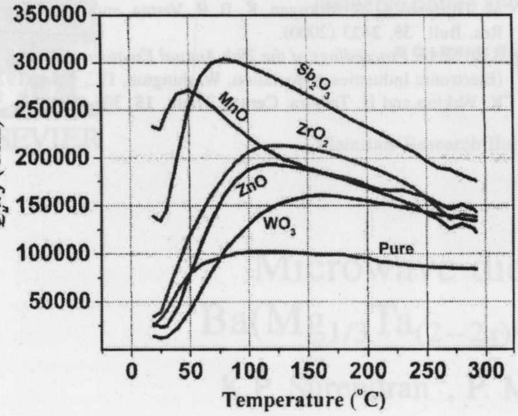

FIG. 4. Variation of unloaded quality factor of pure and doped BMT at cryogenic temperature.

the quality factor at subzero temperatures. Doping with oxygen supplier such as MnO and Sb_2O_3 annihilates the oxygen vacancies in the crystal and annealing increases the cation ordering in the crystal lattice of BMT. These combined effect of these two phenomena resulted in the increase of microwave quality factor on cooling, however, the quality factor of all the samples decreased below 50 K. The quality factor of other doped BMT samples decreases as the temperature of the sample is decreased (see Fig. 4). This can be due to the presence of paramagnetic defects.

IV. CONCLUSIONS

The structural and microwave dielectric property modifications in BMT as a result of doping with several inorganic oxides are investigated. 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 °C for 40 h are $\varepsilon_r = 24.4$, $Q_u x f = 100\,500$ GHz, and $\tau_f = 8$ ppm/°C. With the addition of 0.1 mol % of the divalent dopant MnO, the dielectric properties of BMT were increased to $\varepsilon_r = 26.72$, $Q_u x f = 162\,800$ GHz, and $\tau_f = 6.3$ ppm/°C. The addition of tetravalent dopants 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 ($\varepsilon_r = 25.29$, $Q_u x f = 162\,500$ GHz, and $\tau_f = 4.5$ ppm/°C). The densification and dielectric properties of BMT are 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 $\varepsilon_r = 24.78$, $Q_u x f = 172\,500$ GHz, and $\tau_f = 3.1$ ppm/°C. The addition of hexavalent dopants 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 $\varepsilon_r = 24.9$, $Q_u x f = 144\,500$ GHz, and $\tau_f = 4.1$ ppm/°C.

The microwave quality factor of the doped BMT ceramics shows a proportionate dependence on the ordering of *B*-site cations except for tetravalent dopants. For tetravalent dopants such as ZrO_2, the high quality factor is observed even for samples with a lower-order parameter.

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 the maximum.

The quality factor of as-sintered pure BMT decreases when the sample is cooled below 0 °C. On the other hand when Sb^{5+} and Mn^{2+} doped and annealed BMT the *Q* factor increases on cooling.

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