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Synthesis and characterization of doped $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics

C. JINGA[a*], E. ANDRONESCU[a], S. JINGA[a], A. IOACHIM[b], L. NEDELCU[b], M. I. TOACSAN[b]
[a]*University "Politehnica" of Bucharest, 011061 Bucharest, Romania*
[b]*National Institute of Materials Physics, 077125 Magurele - Bucharest, Romania*

$Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramic is a dielectric material possessing an extremely high $Q \times f$ product value (up to 400 THz) at microwave frequencies. This makes it suitable for applications as a dielectric resonator for wireless communications. BMT samples, prepared by solid-state reaction and doped with Nb^{5+}, V^{5+} or Ga^{3+}, were employed for compositional, structural and morphological characterization. In the present study, we report on the influence of dopants (type and quantity) and sintering temperature on the dielectric properties. It was found that the quality factor is maximum when Nb^{5+} is used as dopant.

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1. Introduction

With the recent progress in the microwave communication systems, microwave dielectric ceramics have become very important for the miniaturization of microwave devices such as filters or antennas [1, 2].

$Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramic possesses excellent dielectric properties: high quality factor ($Q \times f > 400$ THz), moderate dielectric constant ($\varepsilon_r \sim 25$) and small temperature coefficient of resonant frequency ($\tau_f < 5$ ppm/°C), for microwave applications. BMT can have a disordered cubic complex perovskite structure with 1:1 cationic order or a long range ordered (LRO), 1:2 type, trigonal structure. The microwave quality factor of BMT ceramic material depends, especially, on the LRO, with repeated sequence·-Mg-Ta-Ta-·of cations on the perovskite B-site [1, 3, 4].

Because the sinterability of BMT is poor even at high temperatures of 1600 °C, many investigations have been carried out to reduce the sintering temperature of BMT ceramic without deteriorating to much the microwave dielectric properties. Several authors reported improvement in sinterability by the use of sintering aids or dopants [1, 5]. Although they succeeded in improving the dielectric properties of BMT, sintering temperature remained above 1600 °C in most cases.

In this paper, the synthesis of undoped and doped BMT sintered pellets is reported. Nb_2O_5, V_2O_5 and Ga_2O_3 were added in small quantities (≤ 1 mol %) in order to improve the $Q \times f$ product value of BMT ceramic. Different sintering temperatures, in the range (1550 - 1650) °C, were applied. Sinterability, crystalline structure, phase composition and microwave dielectric properties were analysed. Dielectric properties were correlated with structural and morphological features.

2. Experimental

Ceramics with molar formula $Ba(Mg_{1/3}Ta_{2/3})O_3$, undoped and doped with Nb^{5+}, V^{5+} or Ga^{3+} cations, were prepared from high purity reagents by conventional solid-state reaction method. Starting materials consisting of carbonate ($BaCO_3$) and oxides (MgO, Ta_2O_5, Nb_2O_5, V_2O_5, Ga_2O_3) were weighted, homogenised and ball milled using yttria stabilized zirconia balls and absolute ethanol for 2 h, then dried at 50 °C for 3 h. The molar concentration of oxide additives was in the range (0.25 - 1.00) mol % (0.25 %, 0.50 %, 0.75 %, 1.00 %). The precursor mixtures were uniaxial pressed into discs of 20 mm in diameter and calcined at 1250 °C for 2 h, in air. The calcined discs were then subjected to ball milling. The ground powders were granulated with PVA and uniaxial pressed into pellets of 7 mm in diameter under a pressure of 150 MPa. The pellets were thermal treated at three sintering temperatures (1550 °C, 1600 °C, 1650 °C) for 4 h, in air.

In order to study BMT compound formation mechanism, differential scanning calorimetry (DSC) of the precursor powders mixture was performed ranging from room temperature to 1500 °C, under air atmosphere, using a Shimadzu DTA-TA-51H analyzer. Relative density of the sintered pellets was measured by Archimede's method, in alcohol. Structural and compositional analyses were performed by X-ray diffraction (XRD); a Shimadzu XRD 600 diffractometer with Ni filtered Cu-K_α radiation, 2θ

ranging between 10 ° and 70 °, was used. A Hitachi S 2600 N electronic microscope was employed for morphological investigations (SEM).

Hakki-Coleman method was used for dielectric measurements in the microwave domain, at room temperature. A computer aided measurement system containing an HP 8757 C scalar network analyser and an HP 8350 B sweep oscillator was used.

3. Results and discussion

DSC plot (Fig. 1) reveals a small endothermic dip with maximum at 825 °C, heralding the emergence of BMT phase. The endothermic effect is attributed to the $BaCO_3$ decomposition, but also to the $BaCO_3$ partial reaction with Ta_2O_5 or/and MgO. This reaction leads to binary or ternary intermediate compounds. The large endothermic dip with maximum at 1260 °C with a shoulder at 1040 °C represents the main stage in BMT formation. Evidently, the formation of BMT starts at 810 °C, fact that has been comfirmed by the XRD patterns, and takes place in successive stages between 810 °C and 1390 °C. Above 1420 °C, a growth of the crystallinity degree can be noticed.

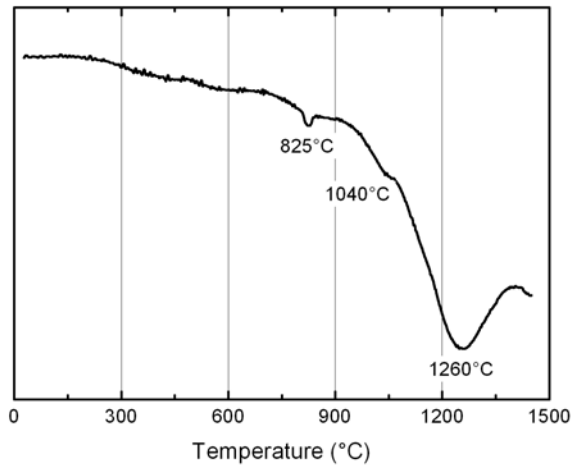

Fig. 1. DSC analysis of the precursor powders mixture.

After the sintering process, the relative density of BMT samples was measured. In figure 2 is presented the dependence of relative density on dopant type and dopant molar concentration for sintering temperature T_s = 1650 °C. The relative density presents the highest values in the case of using V^{5+} as dopant and, generally, it increases with dopant molar concentration increasing. The variation is similar for the other two sintering temperatures. The maximum values appear for V^{5+} doped BMT samples sintered at 1650 °C.

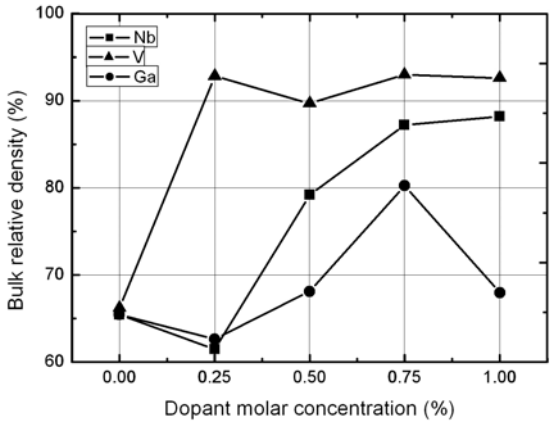

Fig. 2. Bulk relative density of BMT ceramics versus molar concentration of dopant (Nb_2O_5, V_2O_5, Ga_2O_3) for T_s = 1650 °C.

The dependence of relative density on sintering temperature for Nb^{5+} doped BMT samples, presented in figure 3, indicates the increase of density values with sintering temperature increasing. Generally, the relative density increases with Nb^{5+} concentration increasing for the same sintering temperature, except BMT samples with 0.25 mol % Nb_2O_5.

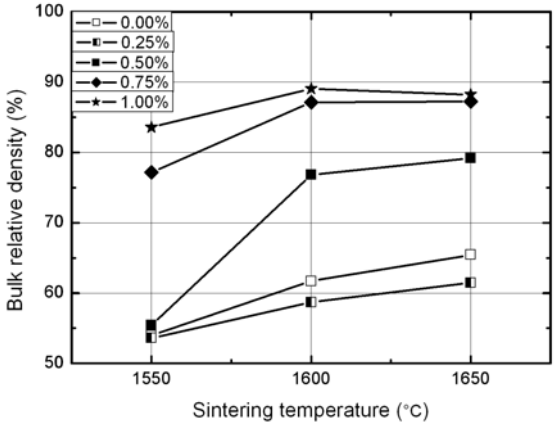

Fig. 3. Bulk relative density of BMT ceramics versus sintering temperature in the case of using Nb^{5+} as dopant.

As a conclusion, BMT samples with a good compactness were obtained by using 1.00 % molar concentration of dopant, like Nb_2O_5 and V_2O_5, and sintering at 1650 °C.

XRD patterns for undoped and doped BMT samples with different amount of added, sintered at 1650 °C are presented in figures 4 - 6. XRD analysis indicates high and sharp peaks corresponding to BMT cubic structure (JCPDS 01-070-9200) and small peaks specific to BMT superstructure with 1:2 cationic ordering [1].

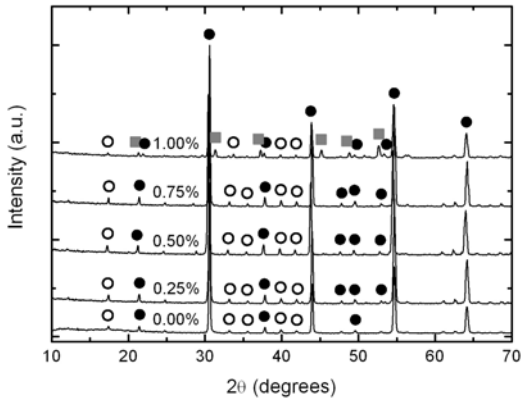

Fig. 4. XRD patterns of Nb^{5+} doped BMT ceramics for T_s = 1650 °C: ●- BMT cubic structure reflections, ○ - BMT superstructure reflections, ■ - unknown phase.

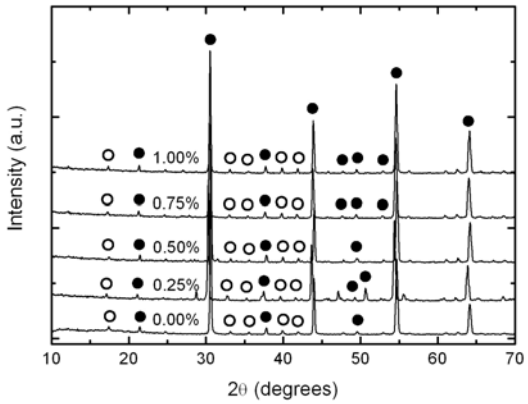

Fig. 5. XRD patterns of V^{5+} doped BMT ceramics for T_s = 1650 °C: ● - BMT cubic structure reflections, ○ - BMT superstructure reflections.

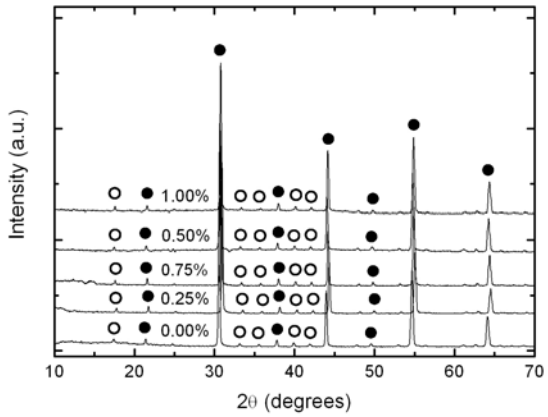

Fig. 6. XRD patterns of Ga^{3+} doped BMT ceramics for T_s = 1650 °C: ● - BMT cubic structure reflections, ○ - BMT superstructure reflections.

The XRD patterns of BMT ceramics sintered at 1550 °C or 1600 °C are similar (Fig. 7). All BMT ceramics are well-structured and exhibits 1:2 LRO domains even for low sintering temperature (1550 °C). Sintering parameters influence the formation and the quantitative ratio between 1:1 and 1:2 ordered domains. For 1.00 mol % added and, especially, for high sintering temperature, small amounts of secondary phases can appear.

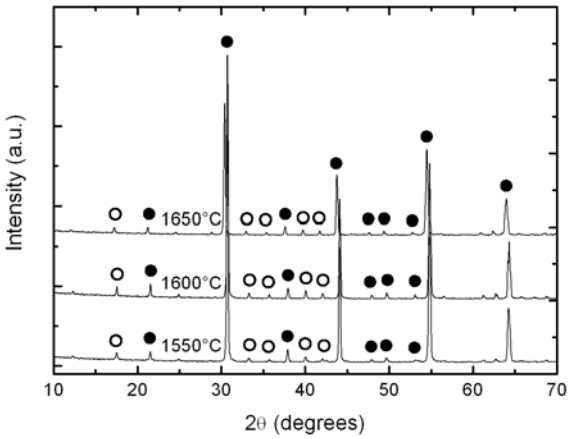

Fig. 7. XRD patterns of BMT ceramics with 0.50 mol % Nb_2O_5: ● - BMT cubic structure reflections, ○ - BMT superstructure reflections.

The microstructure of some undoped and doped BMT ceramics sintered at different temperatures is presented in figures 8 - 14. All BMT samples have a porous structure due to pressing process (uniaxial pressing). Generally, for 1550 °C and 1600 °C sintering temperatures, grains size distribution is monomodal, while for 1650 °C it becomes bimodal; the increase of sintering temperature promotes the granular growth. Grains average dimension increases with dopant molar concentration increasing and sintering temperature increasing. The SEM images reveal spherical or polyhedral grains with rounded edges and corners, with dimensions in the range (0.5 - 4.5) μm. For $T_s \geq 1600$ °C, the SEM images of doped BMT samples show larger grains, smooth surfaces and edges and reduced inter-granular porosity, except Ga^{3+} doped samples. Even at 1650 °C, the Ga^{3+} doped samples show an inhibited grains growth, with sizes in the range (0.1 - 1) μm, and an increased inter-agglomerates porosity.

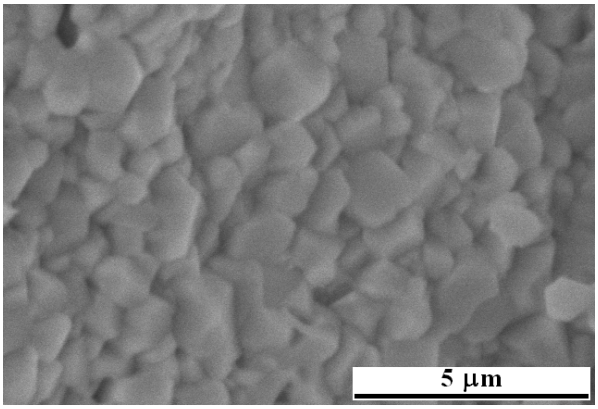

Fig. 8. SEM image of undoped BMT sample sintered at 1650 C / 4h.

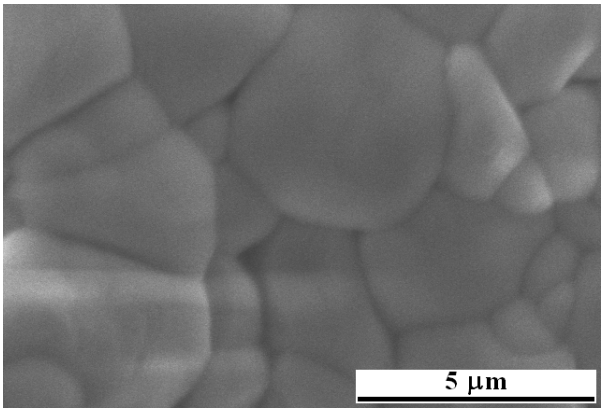

Fig. 11. SEM image of BMT sample with 0.50 mol % Nb_2O_5, sintered at 1650 C / 4h.

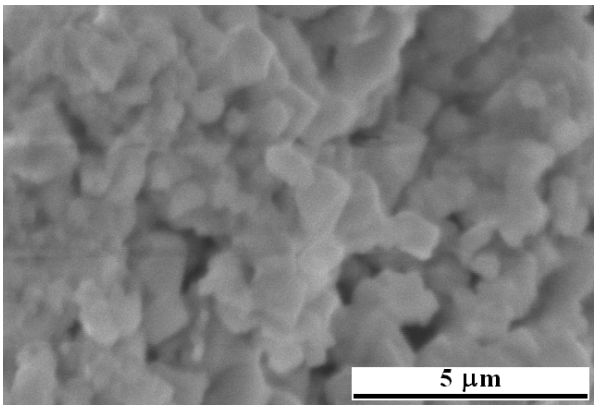

Fig. 9. SEM image of BMT sample with 0.50 mol % Nb_2O_5, sintered at 1550 C / 4h.

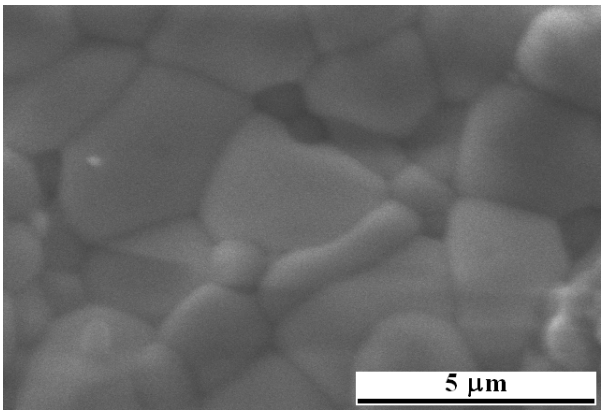

Fig. 12. SEM image of BMT sample with 0.25 mol % Nb_2O_5, sintered at 1650 C / 4h.

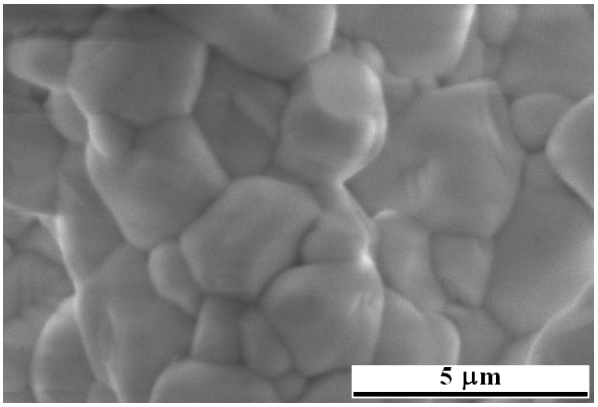

Fig. 10. SEM image of BMT sample with 0.50 mol % Nb_2O_5, sintered at 1600 C / 4h.

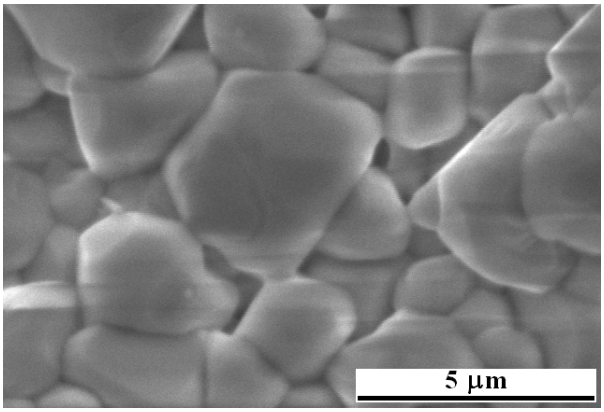

Fig. 13. SEM image of BMT sample with 0.50 mol % V_2O_5, sintered at 1600 C / 4h.

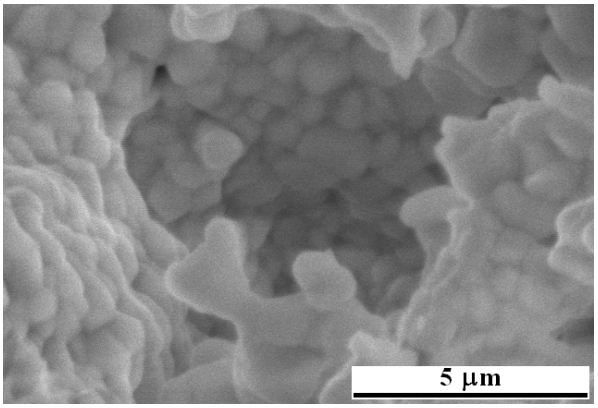

Fig. 14. SEM image of BMT sample with 0.25 mol % Ga_2O_5, sintered at 1650 C / 4h.

Microwave measurements were performed in 5 - 12 GHz frequency range. Figure 15 presents the variation of BMT samples dielectric constant versus dopant type and dopant molar concentration for T_s = 1650 °C, while figure 16 shows the dependence of dielectric constant on sintering temperature for Nb^{5+} doped samples. The dielectric measurements carried out on sintered samples indicate the same trend for dielectric constant as relative density, with maximum values for BMT sample with 0.75 mol % V_2O_5, sintered at 1650 °C. Dielectric constant values are between 9.4 and 22.4.

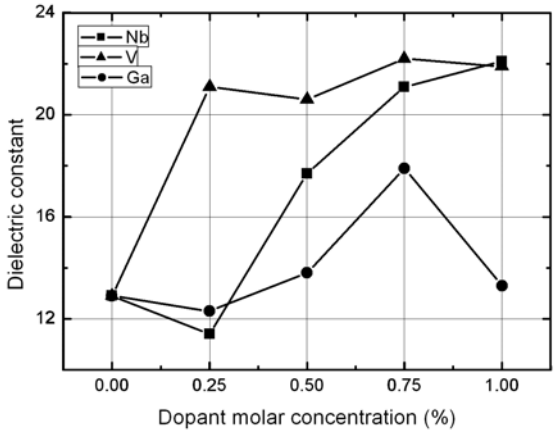

Fig. 15. Dielectric constant of BMT ceramics versus molar concentration of dopant (Nb_2O_5, V_2O_5, Ga_2O_3) for T_s = 1650 °C.

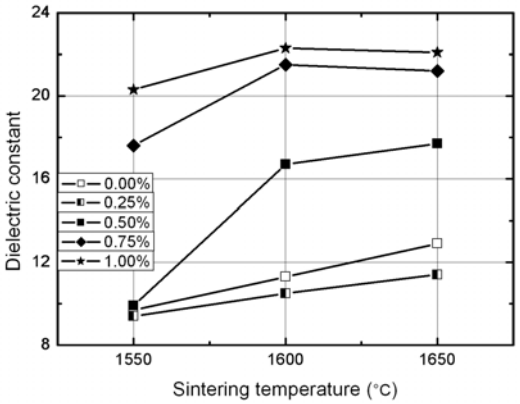

Fig. 16. Dielectric constant of BMT ceramics versus sintering temperature in the case of using Nb^{5+} as dopant.

Figs. 17 and 18 show the variation of $Q \times f$ product value of BMT ceramics versus dopant molar concentration and sintering temperature. The highest value, $Q \times f$ = 220 THz, was obtained for BMT sample with 0.50 mol % Nb_2O_5, sintered at 1650 °C. The other BMT samples present $Q \times f$ values ≤ 150 THz.

The quality factor of complex perovskite microwave materials is very sensitive to a number of different processing and structural variables. It can vary from sample to sample even when they have the same nominal composition due to small differences in the intrinsic crystal structure, microstructure, density and impurity concentration, cationic order and stoichiometry [1].

In some cases, the decrease of quality factor can be attributed to the formation of secondary phases [6]. Still, it is obvious that the highest values for the quality factor are obtained in the case of Nb^{5+} doped BMT samples.

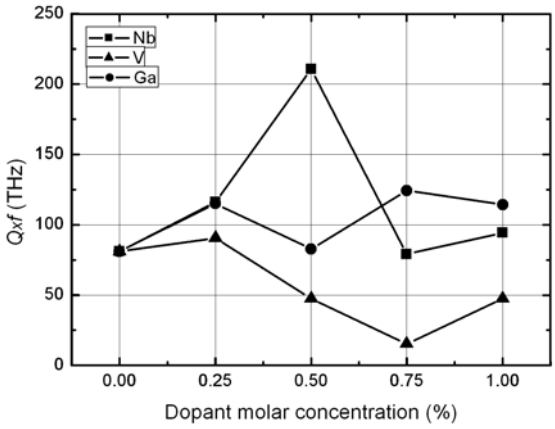

Fig. 17. Q×f product of BMT ceramics versus molar concentration of dopant (Nb_2O_5, V_2O_5, Ga_2O_3) for T_s = 1650 °C.

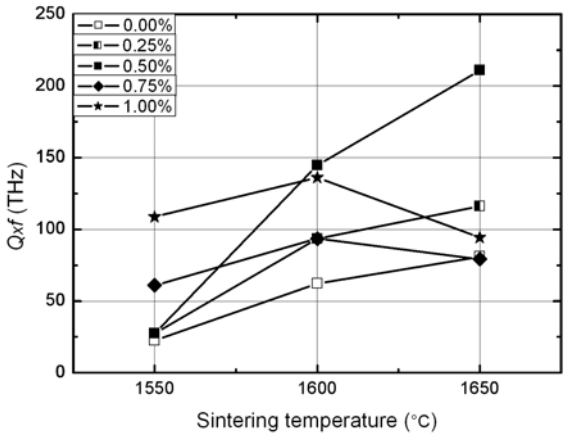

Fig. 18. Q×f product of BMT ceramics versus sintering temperature in the case of using Nb^{5+} as dopant.

4. Conclusions

Undoped and doped BMT ceramics were prepared by a conventional solid-state reaction method and sintered at 1550 C, 1600 C or 1650 C. As dopants, Nb_2O_5, V_2O_5, Ga_2O_3 were used.

Relative density, grains size and dielectric constant increase with dopant molar concentration increasing and sintering temperature increasing.

XRD patterns reveal the formation of BMT compound with small amounts of secondary phases for some samples. All BMT ceramics are well-structured and exhibit 1:2 LRO domains even for low sintering temperature (1550 °C).

For sintering temperatures ≥ 1600 °C, the SEM images of Nb^{5+} and V^{5+} doped BMT samples show larger grains, smooth surfaces and edges, as well as reduced inter-granular porosity.

BMT sample with 0.5 mol % Nb_2O_5, sintered at 1650 °C exhibit the highest value of $Q \times f$ product, ~ 220 THz.

Acknowledgements

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*Corresponding author:jinga_cristina@yahoo.co.uk