Journal of Ceramic Processing Research. Vol. 18, No. 6, pp. 421~424 (2017)

J O U R N A L O F
Ceramic Processing Research

Microwave dielectric properties of $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ ceramics

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Phase formation, microstructure and microwave dielectric properties of Y_2O_3 and TiO_2 doped BMW, i.e., $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$, ceramics were investigated. Up to the composition of x = 0.5, the BMW ceramics having an ordered cubic structure were only observed and no secondary phase such as $BaWO_4$ was detected. As the value of x increased, the lattice parameter increased linearly, implying that a substitutional solid solution occurred. A dense microstructure was observed. The grain shapes was certainly a polyhedron, indicating that the solid phase sintering occurred. As the x value increased, the dielectric constant (ε_r) exhibited a tendency to increase slightly. The quality factor ($Q \times f_0$) sintered at 1700 °C increased up to x = 0.02 and then saturated. All of the compositions sintered at 1700 °C exhibited negative values of the temperature coefficient of resonant frequency (τ_f). The absolute value of τ_f decreased as the x value increased. Dielectric constant (ε_r), quality factor ($Q \times f_0$) and temperature coefficient of resonant frequency (τ_f) of the composition of x = 0.05, i.e., $Ba_2(Mg_{0.40}Y_{0.10}W_{0.45}Ti_{0.10})O_3$, sintered at 1700 °C, were 19.6, 162,794 GHz, and -11.5 ppm/°C, respectively.

Key words: $Ba_2(MgW)O_6$, Ordered perovskite, Polyhedron, Solid phase sintering, Microwave dielectrics.

Introduction

According to the rapid growing of commercial wireless communication industry, many works of microwave dielectric ceramics used for mobile phone, wireless LAN (local area network), GPS (global position satellite), and ITS (intelligent transport system) are being actively conducted [1-3]. To be used for resonators, filters, and oscillators at microwave frequencies, microwave dielectric ceramics should have high dielectric constant (ε_r) for size miniaturization, high quality factor ($Q \times f_0$) for high frequency selectivity and nearly zero temperature coefficient of resonant frequency (τ_f) for thermal stable circuits [4].

Among the various dielectric resonators at microwave frequencies such as $Ba(Mg_{0.33}M_{0.67})O_3$ (where M = Ta^{5+} and Nb^{5+}) with 1 : 2 ordered structure in B-site cations of the perovskite [5, 6], $Ba(Mg_{0.5}W_{0.5})O_3$ (BMW) having the ordered perovskite structure, in which B-site cations are 1 : 1 ordered because their large difference in size and charge has been investigated since Takahashi et al. reported the dielectric properties of BMW with ε_r = 16.7, $Q \times f_0$ = 42,000 GHz, and τ_f = -33.6 ppm/°C [7-10]. Bian et al. reported that the composition of x = 0.3 in the $Ba[\{Mg_{(1-x)/2}Y_{x/3}(V_{Mg})_{x/6}\}W_{1/2}]O_3$ system exhibited the dielectric properties of ε_r = 21.9, $Q \times f_0$ = 133,000 GHz, and τ_f = -2.4 ppm/°C [8]. Lin et al. investigated the microwave dielectric properties of the $(Ba_{1-x}Sr_x)(Mg_{0.5}W_{0.5})O_3$ system, and found that the composition of x = 0.25 showed the dielectric properties of ε_r = 20.6, $Q \times f_0$ = 152,600 GHz, and τ_f = + 24 ppm/°C [9]. Wu et al. reported that the composition of x = 0.02 in the $(1-x)Ba(Mg_{0.5}W_{0.5})O_3$-$(x)Ba(Y_{0.67}W_{0.33})O_3$ system exhibited the dielectric properties of ε_r = 20, $Q \times f_0$ = 160,000 GHz, and τ_f = -21 ppm/°C [10].

In this paper, we have investigated phase formation, microstructure, and microwave dielectric properties of the Y_2O_3 and TiO_2 doped BMW ceramics, i.e., the $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ system ($0.01 \leq x \leq 0.05$).

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Experimental Procedure

Raw powders of $BaCO_3$ (purity 2N5, Sakai Chem. Ind. Co., Ltd., Japan), MgO (purity 2N, High Purity Chem. Co., Ltd., Japan), Y_2O_3 (purity 2N, High Purity Chem. Co., Ltd., Japan), WO_3 (purity 3N, High Purity Chem. Co., Ltd., Japan), and TiO_2 (purity 3N, High Purity Chem. Co., Ltd., Japan) were mixed to prepare the $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ system ($0.01 \leq x \leq 0.05$). The proper ratio of raw powders was ball-milled using zirconia balls and ethyl alcohol in a polyethylene container for 24 hrs. After drying in an oven, the powder mixture was calcined at 1000 °C for 10 hrs using ab alumina crucible, followed by pulverizing, uniaxial pressing at 50 MPa to from a disk-type specimen with 15 mm diameter. The disk-type specimens were sintered at 1600, 1650, 1700 °C for 1 hr, respectively.

The crystalline phases of the sintered specimens were identified by a powder X-ray diffractometer (XRD, D/MAX-2500V/PC, Rigaku, Japan). The microstructure of the sintered specimens was characterized by a field emission scanning electron microscope (FE-SEM, Quanta 250 FEG, FEI, U.S.A.).

Microwave dielectric properties of the specimens were determined using network analyzers. The dielectric constant was measured according to the Hakki-Coleman method using a network analyzer (E5071C, Keysight, U.S.A.). The quality factor was measured by the cavity method using the same equipment. The temperature coefficient of the resonant frequency was measured by the cavity method using a network analyzer (R3767CG, Advantest, Japan) in the temperature from 20 °C to 80 °C.

Results and Discussion

The XRD patterns of Y_2O_3 and TiO_2 doped BMW, i.e., $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$, ceramics sintered at 1700 °C are shown in Fig. 1. The BMW ceramics with an ordered perovskite structure were only observed, suggesting that doped Y_2O_3 and TiO_2 were substituted on Mg^{2+}ion site and W^{6+}ion one, respectively. No other phases such as $BaWO_4$ reported to be formed during the sintering process of the BMW ceramics due to its structural instability at high temperature were observed [8-10]. According to the study of Bian et al. [9, 11], the structure stability of the BMW ceramics was improved and the formation of $BaWO_4$ was suppressed by small amount of Y and rare earth elements such as Sm, Dy, and Yb. It could be suggested that substituted Y^{3+} ion and/or Ti^{4+} one might suppress the formation of $BaWO_4$. But there is no clear evidence about this suggestion and further study is necessary.

The lattice parameter of the Y_2O_3 and TiO_2 doped BMW ceramics is shown in Fig. 2. As the amount of dopants increased, the lattice parameter of the BMW ceramics increased linearly, supporting that a substitutional solid solution occurred. The substitution of Y^{3+} ion larger than Mg^{2+} one, where the ionic radii of Y^{3+} ion and Mg^{2+} one are 0.090 and 0.072 nm, respectively when the coordination number is 6, may lead to the increase of the lattice parameter. The lattice parameter of the undoped BMW ceramics calculated by an extrapolation method could be assumed as 0.81097 nm and this value is reasonable because it was reported as between 0.81072 nm (sintered at 1650 °C) and 0.81115 nm (at 1600 °C).

The microstructure of the Y_2O_3 and TiO_2 doped BMW ceramics was observed by FE-SEM and the

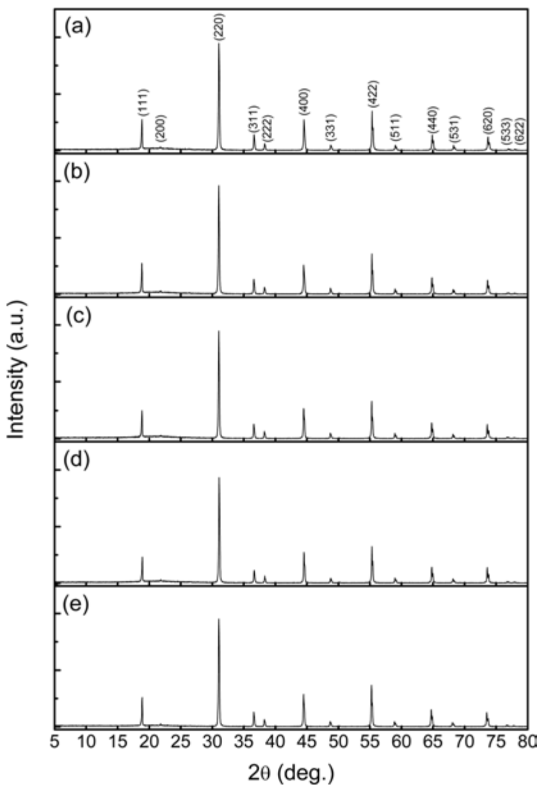

Fig. 1. Powder X-ray diffraction patterns of $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ sintered at 1700 °C for 1 hr, (a) x = 0.01, (b) x = 0.02, (c) x = 0.03, (d) x = 0.04, and (e) x = 0.05.

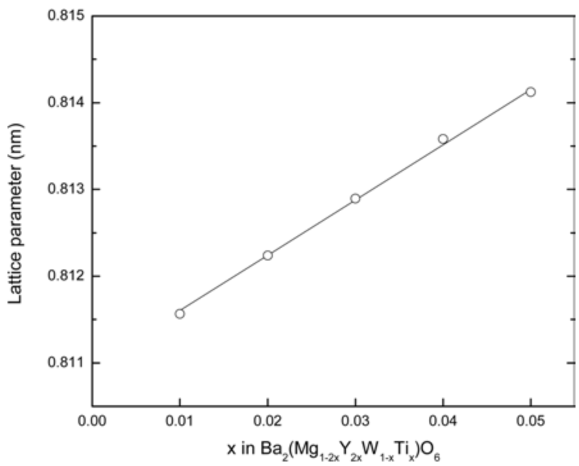

Fig. 2. Lattice parameter of $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ sintered at 1700 °C for 1 hr as a function of x.

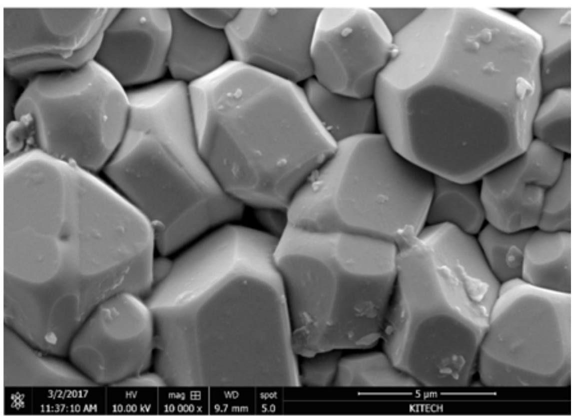

Fig. 3. FE-SEM image of $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ sintered at 1700 °C for 1 hr.

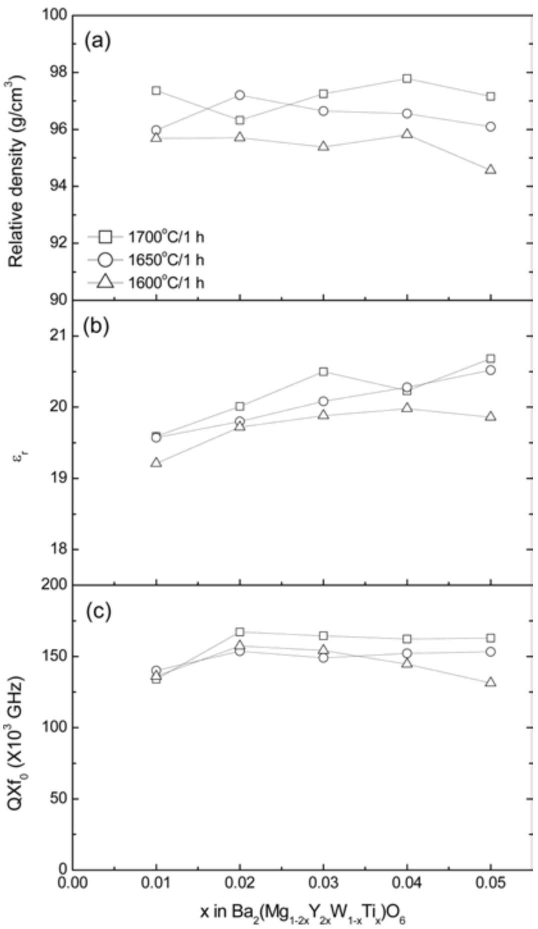

Fig. 4. (a) relative density, (b) dielectric constant (ε_r), and (c) quality factor ($Q \times f_0$) $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$.

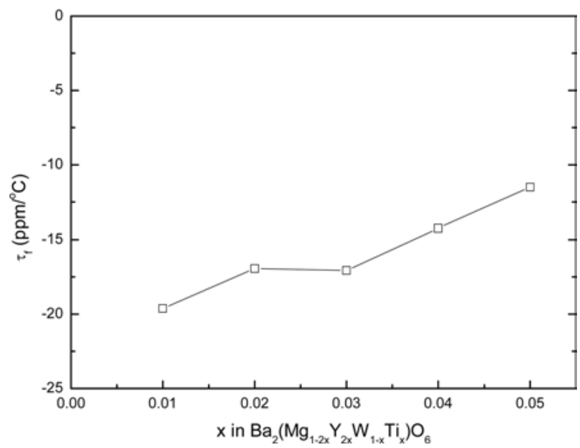

Fig. 5. Temperature coefficient of resonant frequency (τ_f) of $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$ sintered at 1700 °C for 1 hr.

typical microstructure (the composition of x = 0.03 sintered at 1700 °C) is shown in Fig. 3. The FE-SEM image clearly revealed a dense microstructure. The grain shape was certainly a polyhedron, indicating that the solid phase sintering occurred due to the absence of $BaWO_4$ having the low melting point of 1475°C which worked as a sintering aid of the liquid phase [12].

The variations of relative density, dielectric constant (ε_r), and quality factor ($Q \times f_0$) for the Y_2O_3 and TiO_2 doped BMW ceramics sintered at between 1600 °C and 1700 °C is shown in Fig. 4. Table 1 summarizes linear shrinkage, apparent density, lattice parameter (a_0), and microwave dielectric properties of the Y_2O_3 and TiO_2 doped BMW ceramics sintered at 1700 °C. The relative density was calculated using the apparent density. All of compositions, except x = 0.05 sintered at 1600 °C showing 94.6%, exhibited relative densities above 95% of the theoretical density. The ε_r exhibited a tendency to increase slightly as the x value increased, i.e., the dopant concentration increasing. The dielectric constant is mainly influenced by the relative density and the ionic polarizability [11]. Due to the high relative density above 95%, the slight increase of dielectric constant can be ascribed to the increase of ionic polarizability by doping of the Y_2O_3 and TiO_2; the ionic polarizability of Y^{3+}ion ($\alpha_{Y^{3+}} = 3.81$ (Å^3)) is larger than Mg^{2+}ion ($\alpha_{Mg^{2+}} = 1.31$ (Å^3)) whereas the ionic polarizability of Ti^{4+}ion ($\alpha_{Ti^{4+}} = 2.93$ (Å^3)) is similar to that of W^{6+}ion ($\alpha_{W^{6+}} = \sim 3.2$ (Å^3)) [13, 14]. For all of the sintering temperature, the composition of x = 0.02 showed higher value of $Q \times f_0$ than that of x = 0.01. The maximum $Q \times f$ value of 167,130 GHz was obtained at the composition of x = 0.02 sintered at 1700 °C The $Q \times f$ value saturated for the compositions of $x \geq 0.02$ except the compositions sintered at 1600 °C showing a slight decrease due to the relatively low density as shown in Fig. 4(a).

The temperature coefficient of resonant frequency (τ_f) of the Y_2O_3 and TiO_2 doped BMW ceramics

Table 1. Linear shrinkage, apparent density, lattice parameter, and dielectric properties of $Ba(Mg_{0.5-2x}Y_{2x}W_{0.5-x}Ti_x)O_3$ sintered at 1700 °C for 1 hr.

x	Linear shrinkage (%)	Apparent density (g/cm^3)	Lattice parameter, a_0 (nm)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0.01	21.1	97.4	0.81156	19.6	134,037	-19.6
0.02	21.9	96.3	0.81224	20.0	167,130	-16.9
0.03	21.7	97.3	0.81289	20.5	164,408	-17.1
0.04	21.3	97.8	0.81358	20.2	162,295	-14.3
0.05	21.1	97.1	0.81412	20.7	162,795	-11.5

sintered at 1700 °C is shown in Fig. 5. All of the compositions exhibited negative τ_f values from -19.2 ppm/°C for the composition of x = 0.01 to -11.5 ppm/°C for that of x = 0.05. The absolute value of τ_f decreased as the x value increased. Dielectric constant (ε_r), quality factor ($Q \times f_0$) and temperature coefficient of resonant frequency (τ_f) of the composition of x = 0.05, i.e., $Ba_2(Mg_{0.40}Y_{0.10}W_{0.45}Ti_{0.10})O_3$, sintered at 1700 °C, were 19.6, 162,794 GHz, and -11.5 ppm/°C, respectively.

Conclusions

Phase formation, microstructure and microwave dielectric properties of Y_2O_3 and TiO_2 doped BMW, i.e., $Ba_2(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O_6$, ceramics with an ordered perovskite structure were investigated. Up to the composition of x = 0.5, the BMW ceramics having an ordered cubic structure were only observed and no secondary phase such as $BaWO_4$ reported to be formed during the sintering process of the BMW ceramics was detected, implying that doped Y_2O_3 and TiO_2 were successfully substituted on Mg^{2+}ion site and W^{6+}ion one, respectively. As the value of x increased, the lattice parameter increased linearly, supporting that a substitutional solid solution occurred. The lattice parameter of the undoped BMW ceramics calculated by an extrapolation method could be assumed as 0.81097 nm. A dense microstructure was observed. The grain shapes was certainly a polyhedron, indicating that the solid phase sintering occurred. As the x value increased, the dielectric constant (ε_r) exhibited a tendency to increase slightly. The quality factor ($Q \times f_0$) sintered at 1700 °C increased up to x = 0.02 and then saturated for the compositions of x ≥ 0.02. All of the compositions sintered at 1700 °C exhibited negative values of the temperature coefficient of resonant frequency (τ_f). The absolute value of τ_f decreased as the x value increased. Dielectric constant (ε_r), quality factor ($Q \times f_0$) and temperature coefficient of resonant frequency (τ_f) of the composition of x = 0.05, i.e., $Ba_2(Mg_{0.40}Y_{0.10}W_{0.45}Ti_{0.10})O_3$, sintered at 1700 °C, were 19.6, 162,794 GHz, and -11.5 ppm/°C, respectively.

Acknowledgments

This work was financially supported by Ministry of Science, ICT and Future Planning (MSIP) in Korean Government and Korea Industrial Technology Association (KOITA) as “A study on the programs to support collaborative research among industry, academia and research institutes”.

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