Microwave Dielectric Properties of (Ba_{1-x}Na_x)(Mg_{0.5-2y}Ta_{0.5-x}WO_3) Ceramics

Chang-Bae Hong*, Shin Kim**, Sun-Ho Kwon*, and Sang-Ok Yoon*†

*Department of Materials Engineering, Graduate School, Gangneung-Wonju National University, Gangneung 25457, Korea
**Department of Advanced Ceramic Materials Engineering, Gangneung-Wonju National University, Gangneung 25457, Korea
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ABSTRACT

The phase evolution, microstructure, and microwave dielectric properties of (Ba_{1-x}Na_x)(Mg_{0.5-2y}Ta_{0.5-x}WO_3) (0 ≤ x ≤ 0.05) ceramics were investigated. All compositions exhibited a 1:1 ordered perovskite structure. As the value of x increased, the dielectric constant (ε_r) increased from 160,000 GHz, and τ_f = −21 ppm/°C, respectively. In this paper, we investigate the phase evolution, microstructure, and microwave dielectric properties of Na_{0.5-x}O_y, and Ta_{0.5-x}O_{3-y} doped BMW ceramics, i.e., the (Ba_{1-x}Na_y)(Mg_{0.5-2y}Ta_{0.5-x}WO_3) system (0 ≤ x ≤ 0.05).

1. 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. For applications in resonators, filters, and oscillators at microwave frequencies, microwave dielectric ceramics should have high dielectric constant (ε_r) for miniaturization, high quality factor (Q × f) for high frequency selectivity, and nearly temperature coefficient of resonant frequency (τ_f) for thermally stable circuits.

Among the various dielectric resonators at microwave frequencies such as Ba(Mg_{0.5}Ta_{0.5})O_3 (where M = Mg^{2+} and Zn^{2+}) with 1:2 ordered structure of B-site cations in the perovskite, Ba(Mg_{0.3}Ta_{0.7})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 that the dielectric properties of BMW is ε_r = 16.7, Q × f = 42,000 GHz, and τ_f = −33.6 ppm/°C. BIAN et al. investigated the dielectric properties of the (Ba_{1-x}Sr_{x})-(Mg_{y}Ta_{1-2y})O_3 system, and found that the composition of x = 0.25 had the dielectric properties ε_r = 28.6, Q × f = 152,600 GHz, and τ_f = +24 ppm/°C. Wu et al. reported that the composition of x = 0.02 in the (1-x)Ba(Mg_{0.3}Ta_{0.7})O_3-(x)Ba(YSr)O_3 system exhibited the dielectric properties ε_r = 20, Q × f = 160,000 GHz, and τ_f = −21 ppm/°C. In this paper, we investigate the phase evolution, microstructure, and microwave dielectric properties of Na_{0.5-x}O_y, and Ta_{0.5-x}O_{3-y} doped BMW ceramics, i.e., the (Ba_{1-x}Na_y)-(Mg_{0.5-2y}Ta_{0.5-x}WO_3) system (0 ≤ x ≤ 0.05).

2. 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 4N, High Purity Chem. Co., Ltd., Japan), Na_2CO_3 (purity 2N5, Samcheon Chemical Co., Ltd., Japan), WO_3 (purity 4N, High Purity Chem. Co., Ltd., Japan), and Ta_2O_5 (purity 3N, High Purity Chem. Co., Ltd., Japan) were mixed to prepare the (Ba_{1-x}Na_x)(Mg_{0.5-2y}Ta_{0.5-x}WO_3)O_3 system (0 ≤ x ≤ 0.05). The appropriate ratios of raw powders were ball-milled using zirconia balls and ethyl alcohol in a polyethylene container for 24 h. After drying in an oven, the powder mixture was calcined at 900°C for 10 h in an alumina crucible, followed by pulverizing and uniaxial pressing at 50 MPa to form disk-type specimens 15 mm in diameter. The disk-type specimens were sintered at 1700°C for 1 h. 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) at temperatures ranging from 20°C to 80°C.

3. Results and Discussion

The XRD patterns of Na$_2$O-, Y$_2$O$_3$-, and Ta$_2$O$_5$-doped BMW, i.e., (Ba$_{1-x}$Na$_x$)(Mg$_{0.5-2x}$Y$_{2x}$W$_{0.5-x}$Ta$_x$)O$_3$, ceramics are shown in Fig. 1. All compositions show a 1:1 ordered perovskite structure, i.e., an ordered arrangement of MgO$_6$ and WO$_6$ octahedra in the B-site of the perovskite structure. For all compositions, BaWO$_4$ with low melting point of 1475°C was detected as the secondary phase. It has been reported that BaWO$_4$ is usually formed during the sintering process of Ba(Mg$_{0.5}$W$_{0.5}$)O$_3$ owing to its structural instability at high temperatures. Khalyavin et al. proposed the mass balance reaction Ba$_2$MgWO$_6$ → BaWO$_4$ + MgO + BaO as a potential mechanism for the evolution of BaWO$_4$.

The intensity ratio of the (112) plane for BaWO$_4$ to the (220) plane for BMW is shown in Fig. 2. As x increased, the intensity ratio increased, indicating that the addition of the dopants may promote the formation of BaWO$_4$.

The lattice parameters of (Ba$_{1-x}$Na$_x$)(Mg$_{0.5-2x}$Y$_{2x}$W$_{0.5-x}$Ta$_x$)O$_3$ ceramics are shown in Fig. 3. As the amount of dopants increased, the lattice parameters of the BMW ceramics increased linearly, indicating the occurrence of a substitutional solid solution. The substitution of Y$^{3+}$ ions larger than that of Mg$^{2+}$, where the ionic radii of Y$^{3+}$ and Mg$^{2+}$ ions are 0.9 Å and 0.72 Å, respectively, when the coordination number is 6, may lead to the increase of lattice parameters. The lattice parameter of undoped BMW ceramics was measured as 8.1092 Å; this value is reasonable because it was reported as between 8.1072 Å (sintered at 1650°C) and 8.1115 Å (at 1600°C).

The microstructure of the Na$_2$O-, Y$_2$O$_3$-, and Ta$_2$O$_5$-doped BMW ceramics was observed by FE-SEM. The typical microstructures (compositions with x = 0.01, 0.03, and 0.05) are shown in Fig. 4. All the compositions exhibited a dense microstructure with polyhedron-shaped grains. In the case of x = 0.05 composition, large grains were observed. According to the EDS result for the x = 0.05 composition as shown in Fig. 4(d), the large grains were identified as BaWO$_4$. At the sintering temperature of 1700°C, the liquid BaWO$_4$ contributed to densification.

The variations of linear shrinkage, dielectric constant ($\varepsilon_r$), and quality factor (Q × f$_0$) for the Na$_2$O-, Y$_2$O$_3$-, and Ta$_2$O$_5$-doped BMW ceramics are shown in Fig. 5. As x increased, the linear shrinkage increased. The dielectric constant exhibited a tendency to increase slightly as the x value increased.
increased, i.e., with increasing dopant concentration. The dielectric constant is mainly influenced by the relative density and ionic polarizability. The slight increase of the dielectric constant can be attributed to the increase of ionic polarizability by Y\(_{2}\)O\(_3\) and Ta\(_{2}\)O\(_5\) doping; the ionic polarizability of the Y\(^{3+}\) ion (\(\alpha_{Y^{3+}} = 3.81\ (\text{Å}^3)\)) and Ta\(^{5+}\) ion (\(\alpha_{Ta^{5+}} = 4.73\ (\text{Å}^3)\)) is larger than that of the Mg\(^{2+}\) ion (\(\alpha_{Mg^{2+}} = 1.31\ (\text{Å}^3)\)) and W\(^{6+}\) ion (\(\alpha_{W^{6+}} = 3.2\ (\text{Å}^3)\)), respectively.  

The quality factor (\(Q \times f_0\)), i.e., the inverse of the dielectric loss, of undoped BMW was measured as 59,738 GHz, whereas the quality factor of doped BMW has a maximum value of 237,188 GHz in the composition \(x = 0.01\), which gradually decreased with increasing \(x\).

The dielectric losses or the inverse of the quality factor were classified into intrinsic and extrinsic categories.\(^{13}\) The intrinsic dielectric losses depend on the crystal structure, ac field frequency, and temperature. The extrinsic losses increased. 

**Table 1.** Linear Shrinkage, Lattice Parameters, and Dielectric Properties of (Ba\(_{1-x}\)Na\(_x\))(Mg\(_{0.5-2x}\)Y\(_{2x}\)W\(_{0.5-x}\)Ta\(_x\))O\(_3\) Ceramics  

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are associated with the microstructure, e.g., pores, grain size, grain boundaries, and secondary phases. Reaney and Iddles have pointed out that, in reality, extrinsic losses dominate the quality factor.\(^9\) The maximum $Q \times f_0$ value when $x = 0.01$ is attributed to increased density (Fig. 5(a)) and minimum amount of BaWO$_4$ phase (Fig. 2). The temperature coefficient of resonant frequency ($\tau_f$) as a function of the calculated tolerance factor ($t$) using Shannon ionic radii is illustrated in Fig. 6.\(^{10}\) The temperature coefficient of resonant frequency ($\tau_f$) increased monotonically from $-19.32$ ppm/$^\circ$C to $-5.64$ ppm/$^\circ$C as $x$ increased, i.e., tolerance factor decreased. It is generally considered that the temperature coefficient of resonant frequency of perovskite structures is related to the tolerance factor, i.e., the degree of oxygen octahedral tilting.\(^{11}\) In the perovskite structure, the temperature coefficient of resonant frequency was reported to be related to the tilting of BO$_6$. The tilting of YO$_6$ was mainly caused by the employment of Y$^{3+}$ (0.9 Å) with ion radius larger than Mg$^{2+}$ (0.72 Å). The results of linear shrinkage, lattice parameters, and dielectric properties of (Ba$_{1-x}$Na$_x$)(Mg$_{0.5-2x}$Y$_{0.5}$W$_{0.5}$Ta$_3$)O$_{3}$ ceramics are summarized in Table 1.

4. Conclusions

The phase evolution, microstructure, and microwave dielectric properties of (Ba$_{1-x}$Na$_x$)(Mg$_{0.5-2x}$Y$_{0.5}$W$_{0.5}$Ta$_3$)O$_{3}$ (0 $\leq$ $x$ $\leq$ 0.05) ceramics were investigated. In addition to the 1:1 ordered perovskite structure of Ba(Mg$_{0.5}$W$_{0.5}$)O$_3$, a secondary phase of BaWO$_4$ was created. As $x$ increased, the dielectric constant increased slightly and the quality factor showed a tendency to reach the maximum value at $x = 0.01$, and then decreased. The temperature coefficient of resonant frequency ($\tau_f$) increased from $-19.32$ ppm/$^\circ$C to $-5.64$ ppm/$^\circ$C in the positive direction as $x$ increased. The dielectric constant of the $x = 0.05$ composition was 19.9, the quality factor was 128,533 GHz, and the temperature coefficient of resonant frequency was $-5.6$ ppm/$^\circ$C.

REFERENCES

10. J. Y. Wu and J. J. Bian, “Structure Stability and Microwave Dielectric Properties of (1-x)Ba(Mg$_{0.5}$W$_{0.5}$)O$_3$-xBa (Y$_{0.5}$W$_{0.5}$)O$_3$ Ceramics,” J. Am. Ceram. Soc., 97 [3] 880–84 (2014).