Microwave Dielectric Properties of Sr-Substituted $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ Ceramics

Sang-Ok Yoon, Dong-Kyu Choi, Jun-Hyuk Oh, and Shin Kim[†]

Department of Advanced Ceramic Materials Engineering, Gangneung-Wonju National University, Gangneung 25457, Korea

(Received April 13, 2018; Revised May 18, 2018; Accepted May 18, 2018)

ABSTRACT

The phase evolution, microstructure, and microwave dielectric properties of Sr-substituted $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics, i.e., $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ($0 \leq x \leq 0.30$), sintered at 1700°C for 1 h were investigated. All compositions showed a 1 : 1 ordered perovskite structure. In all the compositions, BaWO_4 was detected as the secondary phase. With increasing x in $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, the lattice parameter increased linearly, indicating that a substitutional solid solution occurred. All compositions exhibited a dense microstructure. The value of ϵ_r increased slightly with increasing x . The value of $Q \times f_0$ increased with the increase in x up to $x=0.10$ and reached a saturated value of about 100,000 GHz. The composition for $x=0.20$, i.e., $(\text{Ba}_{0.80}\text{Sr}_{0.20})(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, sintered at 1700°C for 1 h exhibited superior microwave dielectric properties of $\epsilon_r = 19.6$, $Q \times f_0 = 99,358$ GHz, and $\tau_f = 0.0$ ppm/ $^\circ\text{C}$, respectively.

Key words : $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, Ordered perovskite, Dielectric constant, Quality factor, Temperature coefficient of resonant frequency

1. Introduction

Motivated by the rapid growth of the commercial wireless communication industry, research on microwave dielectric ceramics used for mobile phones, wireless local area networks (LAN), global positioning system (GPS), and intelligent transport systems (ITS) is being actively conducted.^{1,2)} For a ceramic to be usable as a dielectric resonator/filter, three key properties need to be optimized; dielectric constant, ϵ_r , should fulfill the condition $20 < \epsilon_r < 50$, dielectric loss or its inverse, the quality factor, $Q > 30,000$ at 1 GHz, and the temperature coefficient of resonant frequency, $\tau_f \sim \pm 3$ ppm/ $^\circ\text{C}$.³⁾ Structural stability and microwave dielectric properties of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ systems with a 1 : 1 ordered perovskite structure have been investigated widely⁴⁻¹⁴⁾ ever since Takahashi *et al.* reported the dielectric properties of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics with $\epsilon_r = 16.7$, $Q \times f_0 = 42,000$ GHz, and $\tau_f = -33.6$ ppm/ $^\circ\text{C}$.⁴⁾ Wu *et al.* reported that for $x = 0.02$, the $(1-x)\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ -(x) $\text{Ba}(\text{Y}_{0.67}\text{W}_{0.33})\text{O}_3$ system exhibited dielectric behavior with $\epsilon_r = 20$, $Q \times f_0 = 160,000$ GHz, and $\tau_f = -21$ ppm/ $^\circ\text{C}$.¹⁰⁾ Bian and Wu reported that for $x = 0.30$, the $\text{Ba}[\{\text{Mg}_{(1-x)/2}\text{Y}_{x/3}(\square_{\text{Mg}})_{x/6}\}\text{W}_{1/2}]\text{O}_3$ ($\square$ refers to the vacancy) system exhibited dielectric behavior with $\epsilon_r = 21.9$, $Q \times f_0 = 133,000$ GHz, and $\tau_f = -2.4$ ppm/ $^\circ\text{C}$.¹³⁾ Lin *et al.* investigated the microwave dielectric properties of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ system with the compositions at wide intervals of $x = 0, 0.25, 0.50$, and 0.75 and found that at $x =$

0.25 , the system exhibited the following dielectric properties: $\epsilon_r = 20.6$, $Q \times f_0 = 152,600$ GHz, and $\tau_f = +24$ ppm/ $^\circ\text{C}$.¹²⁾ In this study, we have investigated the phase evolution, microstructure, and microwave dielectric properties of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ system with $0 \leq x \leq 0.30$ at intervals of 0.05 mol.

2. Experimental Procedure

Raw powders of BaCO_3 (purity 2N5, Sakai Chem. Ind. Co., Ltd., Japan), SrCO_3 (3N, High Purity Chem. Co., Ltd., Japan), MgO (2N, High Purity Chem. Co., Ltd., Japan), and WO_3 (3N, High Purity Chem. Co., Ltd., Japan) were mixed to prepare the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics. Appropriate ratios of the 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 specimen 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 using a powder X-ray diffractometer (XRD, D/MAX-2500V/PC, Rigaku, Japan). The apparent lattice parameter, a , of the cubic structure was calculated using the equation of $a^2 = [(h^2 + k^2 + l^2)\lambda^2]/(4\sin^2\theta)$, where θ is the angle of diffraction of the X-rays from the plane of (hkl) and λ is the wave length of the X-rays. The lattice parameter was determined by plotting the calculated a values versus the Nelson-Riley function $f(\theta)$ ($f(\theta) = 1/2(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$) and determining the y-intercept where the Nelson-Riley function went to zero, i.e.,

[†]Corresponding author : Shin Kim

E-mail : perovskite@gwnu.ac.kr

Tel : +82-33-640-2360 Fax : +82-33-640-2244

at $\theta = \pi/2$. Microstructure of the sintered specimens was characterized by a field emission scanning electron microscope (FE-SEM, Quanta 250 FEG, FEI, U.S.A.). The microwave dielectric properties of the specimens were determined using network analyzers. The dielectric constant was measured by Hakki-Coleman method using a network analyzer (E5071C, Keysight, U.S.A.). The quality factors of the sintered specimens were measured by the cavity method using the same equipment. The temperature coefficient of resonant frequency was measured by the cavity method using a network analyzer (R3767CG, Advantest, Japan) in the temperature range of 20°C to 80°C.

3. Results and Discussion

The powder X-ray diffraction patterns of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30) ceramics sintered at 1700°C 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 B-site of the perovskite structure. In all the compositions, BaWO_4 is detected as the secondary phase. It was reported that BaWO_4 is usually formed during the sintering of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ due to its structural instability at high temperatures.^{5,8-10} Khalyavin *et al.* suggested a mass balance reaction of $\text{Ba}_2\text{MgWO}_6 \rightarrow \text{BaWO}_4 + \text{MgO} + \text{BaO}$ as a possible mechanism for the formation of BaWO_4 .⁵ The peak at $2\theta \sim 42.9^\circ$ may correspond to the (200) plane of MgO (ICDD number 45-0946) and/or the (204) plane of BaWO_4 (ICDD number 43-0646). There was no inter-dependency between the amount of BaWO_4 calculated from the intensity ratio of $I_{(110)} \text{BaWO}_4 / I_{(220)} \text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ and value of x in $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$. The minimum value of the intensity ratio $I_{(110)} \text{BaWO}_4 / I_{(220)} \text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ is obtained for the composition with $x = 0.10$. The presence of MgO or Mg -rich phases in the sintered specimens of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics has been previously reported.^{5,8} Similar to other studies, BaO is not detected in any of the compositions in this study. It was pre-

Fig. 1. Powder X-ray diffraction patterns of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics.

Fig. 2. Lattice parameter of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics as a function of x .

viously suggested that BaO might exist in the amorphous state or as a solid solution with $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ or BaWO_4 .^{6,8}

The lattice parameters of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics are shown in Fig. 2. With increasing x in $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, the lattice parameter decreases linearly indicating that a substitutional solid solution occurs. The substitution of Ba^{2+} ion by a smaller Sr^{2+} ion, where the ionic radii of Sr^{2+} ion and Ba^{2+} ion are 1.44 Å and 1.61 Å, respectively, when the coordination number is 12, may be the cause for the decrease in the value of lattice parameter.¹⁵ The lattice parameter of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ sintered at 1700°C in this study is 8.1092(3) Å and it was reported as between 8.1072 Å (sintered at 1650°C) and 8.1115 Å (sintered at 1600°C).⁵ The typical FE-SEM images of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics (the compositions with $x = 0, 0.10$, and 0.30) are shown in Fig. 3. All the compositions exhibit a dense microstructure and the grain shape is certainly a polyhedron.

The linear shrinkage, the dielectric constant (ϵ_r), and the quality factor ($Q \times f_0$) are illustrated in Fig. 4. The linear shrinkage of the composition for $x = 0$, i.e., $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, is much lower than that of other compositions. The linear shrinkage increases with the increase of x except for the composition with $x = 0.25$, implying that the sinterability of $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics is improved by the Sr substitution. In addition, it is considered that its sinterability is improved by the liquid phase sintering due to the formation of BaWO_4 having a low melting point of 1430°C.¹²

The variation of ϵ_r is similar to that of the linear shrinkage. The value of ϵ_r for the composition with $x = 0$ is 17.3 and it was reported as 16.7 (sintered at 1500°C.⁴), 17.6 (sintered at 1600°C⁵), and 18.9 (sintered at 1575°C¹²) earlier. The value of ϵ_r increases slightly with increasing x except for the composition with $x = 0.10$. It is considered that the relatively high ϵ_r of the composition with $x = 0.10$ may be due to the presence of small amount of BaWO_4 having a low ϵ_r of 8.1¹⁶ as mention above. The value of $Q \times f_0$ for $\text{Ba}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics is 59,738 GHz, which is higher than that reported by Takahashi *et al.*⁴) and lower than that

Fig. 3. FE-SEM images of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics; (a) $x = 0$, (b) $x = 0.10$, and (c) $x = 0.30$.

reported by Lin *et al.*¹²⁾ The value of $Q \times f_0$ increases with increase in x up to $x = 0.10$ and reaches a saturated value of about 100,000 GHz. It is considered that the increase in $Q \times f_0$ may be related to the improvement in sinterability owing to the substitution of Ba^{2+} ion by Sr^{2+} ion and the liquid phase sintering as mentioned above. The dielectric losses or the inverse of the quality factor are generally classified into intrinsic and extrinsic categories. The intrinsic dielectric losses depend on the crystal structure, ac field frequency and temperature. The extrinsic losses are associated with the microstructure, e.g., pores, grain boundaries, and secondary phases.⁹⁾ Reany and Iddles have pointed out that, in reality, extrinsic losses dominate the quality factor.³⁾

The temperature coefficient of resonant frequency (τ_f) as a

Fig. 4. Linear shrinkage, dielectric constant (ϵ_r), and quality factor ($Q \times f_0$) of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics as a function of x .

function of the calculated tolerance factor (t) using Shannon ionic radii is illustrated in Fig. 5.¹⁵⁾ The value of τ_f for the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramics increases from a negative value to a positive one with increasing x . It was reported that τ_f is related to the temperature coefficient of the dielec-

Fig. 5. Temperature coefficient of resonant frequency (τ_f) of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ ceramic as a function of tolerance factor.

tric constant (ϵ_r) and the linear thermal expansion coefficient (α_L) by $\tau_f = -(\epsilon_r/2 + \alpha_L)$.³⁾ In addition an overall empirical correlation between ϵ_r and the tolerance factor of the perovskite structure (t) is given by $t = (R_A + R_O)/[\sqrt{2}(R_B + R_O)]$ where R_A , R_B , and R_O are the ionic radii of A, B, and oxygen ions in the ABO₃ perovskite structure, has been established by Reaney *et al.*¹⁷⁾ The value of τ_f in this study ranges from -27.3 ppm/°C for the composition with $x = 0$, which is similar to that reported by Lin *et al.*,¹²⁾ to 10.3 ppm/°C for the composition with $x = 0.30$ and zero value of τ_f is obtained for the composition with $x = 0.20$. The composition with $x = 0.20$, i.e., (Ba_{0.80}Sr_{0.20})(Mg_{0.5}W_{0.5})O₃, sintered at 1700°C for 1 h, exhibits superior microwave dielectric properties of $\epsilon_r = 19.6$, $Q \times f_0 = 99,358$ GHz, and $\tau_f = 0.0$ ppm/°C.

4. Conclusions

The phase evolution, microstructure, and microwave dielectric properties of Sr-substituted Ba(Mg_{0.5}W_{0.5})O₃ ceramics, i.e., (Ba_{1-x}Sr_x)(Mg_{0.5}W_{0.5})O₃ ($0 \leq x \leq 0.30$), sintered at 1700°C for 1 h were investigated. All compositions showed a 1 : 1 ordered perovskite structure. In all the compositions, BaWO₄ was detected as the secondary phase. With increasing x in (Ba_{1-x}Sr_x)(Mg_{0.5}W_{0.5})O₃, the lattice parameter increased linearly, indicating that a substitutional solid solution occurred. All compositions exhibited a dense microstructure and the grain shape was confirmed to be a polyhedron. The linear shrinkage increased with the increase in x except for the composition with $x = 0.25$, implying that the sinterability of Ba(Mg_{0.5}W_{0.5})O₃ ceramics was improved by the substitution of Sr. The value of ϵ_r increased slightly with increasing x except for the composition with $x = 0.10$. The value of $Q \times f_0$ increased with increase in x up to $x = 0.10$ and reached a saturated value about 100,000 GHz. The composition with $x = 0.20$, i.e., (Ba_{0.80}Sr_{0.20})(Mg_{0.5}W_{0.5})O₃, sintered at 1700°C for 1 h exhibited superior microwave dielectric properties with $\epsilon_r = 19.6$, $Q \times f_0 = 99,358$ GHz, and $\tau_f = 0.0$ ppm/°C, respectively.

Acknowledgments

This study was supported by Gangneung-Wonju National University.

REFERENCES

1. H. Ohsato, T. Tsunooka, M. Ando, Y. Ohishi, Y. Miyauchi, and K. Kakimoto, "Millimeter-Wave Dielectric Ceramics of Alumina and Forsterite with High Quality Factor and Low Dielectric Constant," *J. Korean Ceram. Soc.*, **40** [4] 350-53 (2003).
2. H. Ohsato, M. Ando, and T. Tsunooka, "Synthesis of Forsterite with High Q and Near Zero TC_f for Microwave/Millimeterwave Dielectrics," *J. Korean Ceram. Soc.*, **44** [11] 597-606 (2007).

3. I. M. Reaney and D. Iddles, "Microwave Dielectric Ceramics for Resonators and Filters in Mobile Phone Networks," *J. Am. Ceram. Soc.*, **89** [7] 2063-72 (2006).
4. H. Takahashi, K. Ayusawa, and N. Sakamoto, "Microwave Dielectric Properties of Ba(Mg_{1/2}W_{1/2})O₃-BaTiO₃ Ceramics," *Jpn. J. Appl. Phys.*, **36** [9A] 5597-99 (1997).
5. D. D. Khalyavin, J. Han, A. M. R. Senos, and P. Q. Mantas, "Synthesis and Dielectric Properties of Tungsten-Based Complex Perovskites," *J. Mater. Res.*, **18** [11] 2600-7 (2003).
6. J. J. Bian, K. Yan, and Y. F. Dong, "Microwave Dielectric Properties of A_{1-3x/2}La_x(Mg_{1/2}W_{1/2})O₃ (A=Ba, Sr, Ca; $0.0 \leq x \leq 0.05$) Double Perovskites," *Mater. Sci. Eng. B*, **147** [1] 27-34 (2008).
7. J. J. Bian, Y. F. Dong, and G. X. Song, "Structural Evolution and Microwave Dielectric Properties of (1-x)BaZn_{1/3}Nb_{2/3}O_{3+x}BaMg_{1/2}W_{1/2}O₃ Ceramics," *J. Electroceram.*, **22** [4] 390-94 (2009).
8. J. Y. Wu and J. J. Bian, "Structure Stability and Microwave Dielectric Properties of Double Perovskite Ceramics - Ba₂Mg_{1-x}Ca_xWO₆ ($0.0 \leq x \leq 0.15$)," *Ceram. Int.*, **38** [4] 3217-25 (2012).
9. J. Y. Wu and J. J. Bian, "Effect of Nonstoichiometry on the Microstructure and Microwave Dielectric Properties of Ba(Mg_{1/2}W_{1/2})O₃ Ceramics," *Ceram. Int.*, **39** [4] 3641-49 (2013).
10. J. Y. Wu and J. J. Bian, "Structure Stability and Microwave Dielectric Properties of (1-x)Ba(Mg_{1/2}W_{1/2})O₃ + xBa(Y_{2/3}W_{1/3})O₃ Ceramics," *J. Am. Ceram. Soc.*, **97** [3] 880-84 (2014).
11. J. Bian, J. Wu, R. Uvic, C. Karthik, and Y. Wu, "Structural Stability and Microwave Dielectric Properties of (1-x)Ba(Mg_{1/2}W_{1/2})O₃-xBa(RE_{2/3}W_{1/3})O₃ (RE = Sm, Dy, Y, Yb) Solid Solutions," *J. Eur. Ceram. Soc.*, **35** [5] 1431-39 (2015).
12. Y.-J. Lin, S.-F. Wang, S.-H. Chen, Y.-L. Liao, and C.-L. Tsai, "Microwave Dielectric Properties of (Ba_{1-x}Sr_x)(Mg_{0.5}W_{0.5})O₃ Ceramics," *Ceram. Int.*, **41** [7] 8931-35 (2015).
13. J. J. Bian and J. Y. Wu, "Structure and Microwave Dielectric Properties of B-site Deficient Double Perovskite - Ba[(Mg_{(1-x)/2}Y_{x/6}□_{x/6})W_{1/2}]O₃," *Ceram. Int.*, **42** [2] 3290-95 (2016).
14. S. Kim, C.-B. Hong, S.-H. Kwon, and S.-O. Yoon, "Microwave Dielectric Properties of Ba₂(Mg_{1-2x}Y_{2x}W_{1-x}Ti_x)O₆ Ceramics," *J. Ceram. Process. Res.*, **18** [6] 421-24 (2017).
15. R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.*, **A32** 751-67 (1976).
16. S. H. Yoon, D.-W. Kim, S.-Y. Cho, and K. S. Hong, "Investigation of the Relations between Structure and Microwave Dielectric Properties of Divalent Metal Tungstate Compounds," *J. Eur. Ceram. Soc.*, **26** [10-11] 2051-54 (2006).
17. I. M. Reaney, E. L. Colla, and N. Setter, "Dielectric and Structural Characteristics of Ba- and Sr- based Complex Perovskites as a Function of Tolerance Factor," *Jpn. J. Appl. Phys.*, **33** [7A] 3984-90 (1994).