Microwave dielectric properties of cation-deficient perovskite $Ba_2La_2ZnW_2O_{12}$ ceramics

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The microwave dielectric properties of $Ba_2La_2ZnW_2O_{12}$ ceramics were investigated with a view to the use of such ceramics in mobile communication. $Ba_2La_2ZnW_2O_{12}$ ceramics were prepared using the conventional solid-state method with various sintering temperatures. $Ba_2La_2ZnW_2O_{12}$ is the main crystalline phase, which is accompanied by small amounts of $BaWO_4$ as second phases. Dielectric constants (ε_r) of 21.0-21.6 and a quality factor ($Q \times f$) of 18,700-38,900 GHz were obtained at sintering temperatures in the range 1400-1475 ^{O}C for 2 h. A dielectric constant (ε_r) of 21.6, a quality factor ($Q \times f$) of 38,900 GHz, and a temperature coefficient of resonant frequency (τ_f) of -104 ppm/ ^{O}C were obtained when $Ba_2La_2ZnW_2O_{12}$ ceramics were sintered at 1450 ^{O}C for 2 h.

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Keywords: $Ba_2La_2ZnW_2O_{12}$, Dielectric constant, Quality factor, Temperature coefficient of resonant frequency

1. Introduction

The use of microwave ceramics in resonators, filters, and other devices in mobile communication systems has been increasing rapidly in the recent decade. Numerous works have focused on developing excellent microwave dielectric materials to promote device miniaturization and system stability. Materials that are to be utilized in microwave devices must have three dielectric characteristics - a high dielectric constant, a high quality factor, and a near-zero temperature coefficient of resonant frequency. These enable small devices with low loss and high temperature stability, respectively, to be fabricated [1,2].

The benefits of using complex perovskite ceramics of B-site cation-deficient perovskite ceramics $A_nB_{n-1}O_{3n}$ (n=4-8) are reportedly associated with their excellent dielectric properties at microwave frequencies. A dielectric constant of 44, a $Q \times f$ of 9,000 GHz and a temperature coefficient of resonant frequency of -100 ppm/ ^{O}C was obtained for $Ba_3LaNb_3O_{12}$ ceramics [3]. $Ba_3LaTa_3O_{12}$ have been obtained with a dielectric constant of 36.8, a $Q \times f$ of 21,965 GHz and a temperature coefficient of resonant frequency of -49.6 ppm/ ^{O}C [4]. $Ba_2La_2TiNb_2O_{12}$ ceramics had a dielectric constant of 42.7, a $Q \times f$ of 31,130 GHz, and a temperature coefficient of resonant frequency of -4.2 ppm/ ^{O}C [5].

According to previous studies, the structure of B-site cation-deficient $Ba_2La_2ZnW_2O_{12}$ ceramics were described as close-packed $[AO_3]$ arrays in a sequence of $(hcch)_3$ [6]. This B-site cation-deficient $Ba_2La_2ZnW_2O_{12}$ ceramics was identified with a rhombohedral crystal structure belongs to *R3m* space group. However, no technical information on the microwave dielectric properties of $Ba_2La_2ZnW_2O_{12}$ ceramics is available in the published literature. This fact motivates this investigation of the microwave dielectric properties of $Ba_2La_2ZnW_2O_{12}$ ceramics.

In this paper, $Ba_2La_2ZnW_2O_{12}$ ceramics were synthesized herein using the conventional mixed-oxide method. The effects of the sintering temperature on the microwave dielectric properties of $Ba_2La_2ZnW_2O_{12}$ ceramics were explored. The dielectric properties of the

$Ba_2La_2ZnW_2O_{12}$ ceramics at microwave frequencies varied with the sintering temperature. These microwave dielectric properties were analyzed by densification, X-ray diffraction (XRD), and by making microstructural observations.

2. Experimental procedure

The starting raw chemicals were highly pure $BaCO_3$ (99.9%) (from NOAH CHEMICALS), ZnO (99.0%) (from SHOWA CHEMICAL CO.,LTD.), La_2O_3 (99.9%) (from Acros Organics Co., Ltd.), and WO_3 (99.8%) (from STREM CHEMICALS, INC.) powders. The compound $Ba_2La_2ZnW_2O_{12}$ specimens were prepared by the conventional mixed-oxide method. The raw material was weighed out in stoichiometric proportions, ball-milled in alcohol, dried, and then calcined at temperatures of 1250 °C for 2 h. The calcined powder was re-milled for 12 h using polyvinylalcohol (PVA) solution as a binder. The obtained powder was then crushed into a fine powder through a sieve with a 200 mesh. The obtained fine powder was then axially pressed at 2000 kg/cm^2 into pellets with a diameter of 11 mm and a thickness of 6 mm. The specimens thus obtained were then sintered at temperatures of 1400 to 1475 °C for 2 h in air. Both the heating rate and the cooling rate were set to 10 °C /min.

Following sintering, the phases of the samples were investigated by X-ray diffraction. An X-ray Rigaku D/MAX-2200 data was used with Cu$K\alpha$ radiation (at 30 kV and 20 mA) and a graphite monochromator in a 2θ range of 10° -60°. Scanning electron microscopy (SEM; JEOL JSM-6500F) was utilized to elucidate the microstructures of the specimens. The grain sizes were measured by line intercept method. Their apparent densities were measured using the Archimedes method with distilled water as the liquid. The microwave dielectric properties of the specimens were measured using the postresonator method that was developed by Hakki and Coleman [7]. The Agilent E5071C network analyzer was used to identify the TE_{011} and TE_{012} resonant frequency of the dielectric resonator, and the dielectric constant and quality factor were calculated. The conductor loss of the end plates must be subtracted to obtain the quality factor. For this purpose, two specimens with different heights were prepared, where the height of the specimen for the TE_{012} mode measurement was twice as large as that of the specimen for the TE_{011} mode. The postresonator scheme utilizes a cylindrical specimen of diameter D and length L. The specimens that were used to measure microwave dielectric properties had an aspect ratio, D/L, of approximately 1.6, which is in the range that was specified by Kobayashi and Katoh [8]. The scheme for measuring τ_f was the same as that for measuring the dielectric constant. The test cavity was placed in a chamber and the temperature was increased from 25 to 75 °C. The τ_f value (ppm/ °C) can be determined by noting the change in resonant frequency,

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

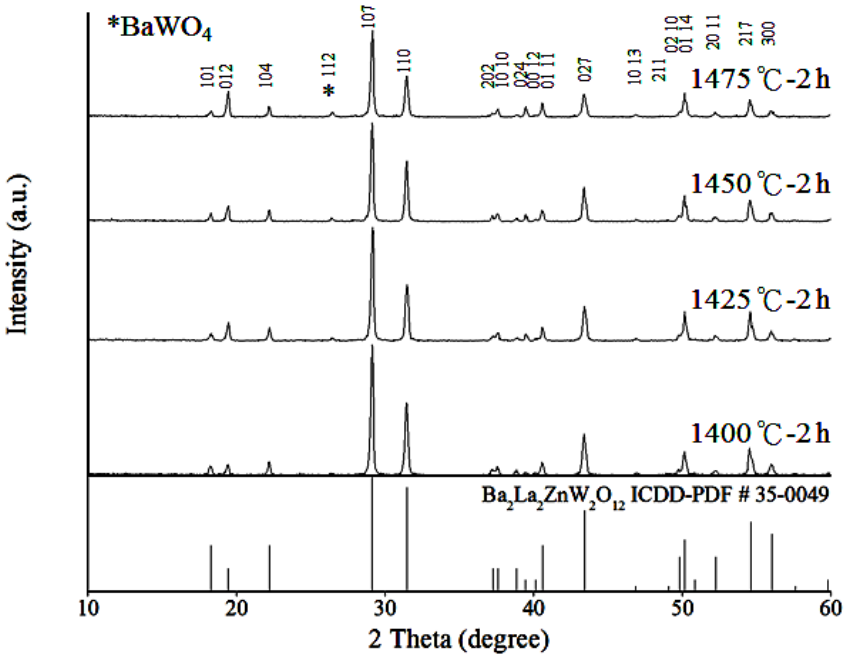

Fig. 1. X-ray diffraction patterns of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h. (:$BaWO_4$)*

Table 1. Main phase, second phase and average grain size of $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 ^{O}C for 2 h

Sintering temperature (^{O}C)	Main phase (%)	Second phase (%)	Average grain size (μm)
1400	98.99	1.01	1.09
1425	97.62	2.38	1.28
1450	96.23	3.77	1.46
1475	94.35	5.65	2.12

3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h. Clearly, $Ba_2La_2ZnW_2O_{12}$ is the main crystalline phase, which is accompanied by small amounts of $BaWO_4$ as second phases. $BaWO_4$ with a tetragonal crystal structure (ICDD-PDF #43-0646) was identified. As displayed in Fig. 1, the (1 1 2) peak of the $BaWO_4$ ceramic was at 26.450°. This appearance of $BaWO_4$ is associated with the moisture content in the starting raw materials of La_2O_3. Table 1 shows the amounts of main and second phase of the specimens that were sintered at 1400-1475 ^{O}C for 2 h. The amount of the main phase was evaluated from strongest lines of both main and second phases,

$$Ba_2La_2W_2O_{12} = \frac{I_{A(107)}}{I_{A(107)}+I_{B(112)}} \times 100 \qquad (2)$$

where I_A and I_B are the strongest lines of $Ba_2La_2ZnW_2O_{12}$ (1 0 7) and $BaWO_4$ (1 1 2), respectively. The amount of the main phase decreased from 98.99 % to 94.35 % as the temperature of sintering for 2 h increased from 1400 to 1475 ^{O}C. The formation of the second phase of $BaWO_4$ may affect the microwave dielectric properties of dielectric $Ba_2La_2ZnW_2O_{12}$ ceramics. $BaWO_4$ ceramics had a constant (ε_r) of 8.2, a quality factor ($Q \times f$) of 21,120 GHz and a temperature coefficient of resonant frequency (τ_f) of -17 ppm/ ^{O}C were obtained [9].

Fig. 2 presents the microstructures of $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered under various temperatures for 2 h. The $Ba_2La_2ZnW_2O_{12}$ ceramics were not dense, and grains did not grow sintering at 1400 ^{O}C for 2 h. When the sintering temperature was increased from 1400 to 1475 ^{O}C

for 2 h, the pores were eliminated and densification occurred. Comparing the microstructures of $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered under various sintering temperatures revealed that the grain size increased with the sintering temperature. Table 1 shows the average grain size of the specimens that were sintered at 1400-1475 ^{O}C for 2 h. The average grain size of $Ba_2La_2ZnW_2O_{12}$ ceramics increased from 1.09 to 2.12 μm as sintering temperature increased from 1400 to 1475 ^{O}C.

Fig. 3 displays the apparent densities and relative densities of the $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 ^{O}C for 2 h.

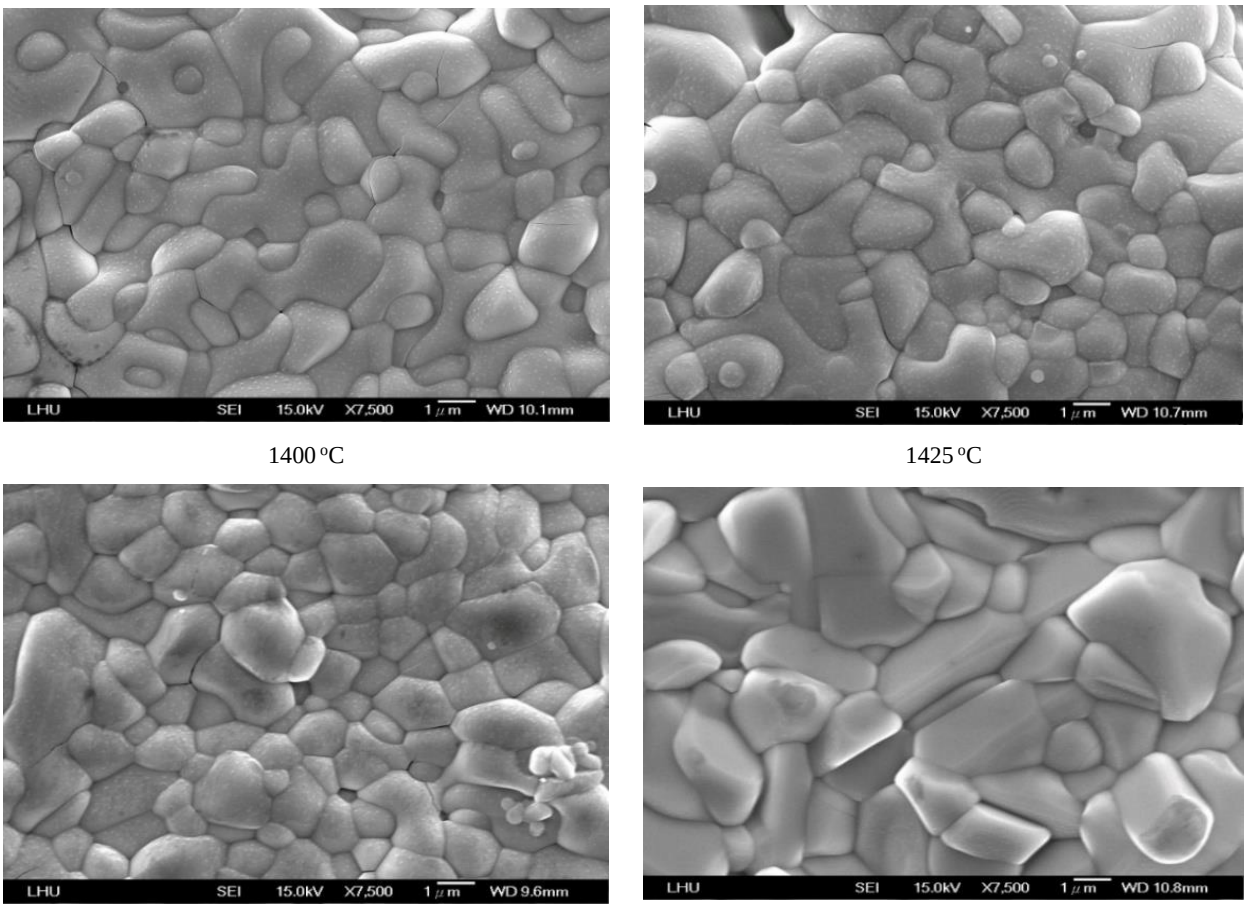

Fig. 2. Microstructures of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered under various sintering temperatures

Of the $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 ^{O}C for 2 h, the one that was sintered at 1475 ^{O}C for 2 h had the highest apparent density. $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1450 ˚C for 2 h had a maximum apparent density of 7.43 g/cm^3. The theoretical density of the $Ba_2La_2ZnW_2O_{12}$ ceramics can be calculated by following equation:

$$D_{composite} = v_1 D_1 + v_2 D_2 \quad (3)$$

where $D_{composite}$ is the calculated theoretical density of the ceramic system, v_1 and v_2 are the volume fraction of $Ba_2La_2ZnW_2O_{12}$ and $BaWO_4$, respectively, and D_1 and D_2 are the theoretical density of $Ba_2La_2ZnW_2O_{12}$ and $BaWO_4$, respectively. The theoretical densities of $Ba_2La_2ZnW_2O_{12}$ and $BaWO_4$ are 7.62 and 6.392 g/cm^3, respectively. The theoretical densities decreased from 7.61 to 7.55 g/cm^3 as sintering temperature increased from 1400 to 1475 ^{O}C. Relative densities of 97.0%-98.4% were obtained for $Ba_2La_2ZnW_2O_{12}$ ceramics at sintering temperatures of

1400-1475 ^{O}C for 2 h. The increase in relative density with sintering temperature may have been caused by the decrease in the number of pores and uniform grain growth, as presented in Fig. 2.

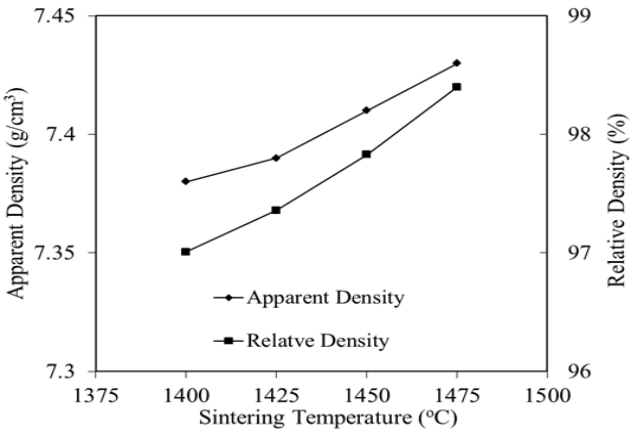

Fig. 3. Apparent densities and relative densities of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h

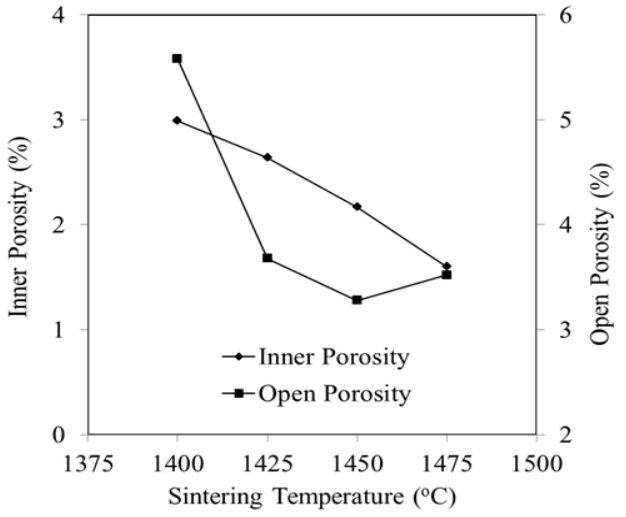

Fig. 4. Inner porosities and open porosities of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h

Fig. 4 displays the porosities of inner and open pores of the $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475˚C for 2 h. The porosities of inner pores decreased from 2.99 % to 1.60 % as sintering temperature increased from 1400 to 1475 ˚C. The percentage open porosity can be calculated [10]:

$$P = \frac{W-D}{W-S}, \quad (4)$$

where P is the percentage open porosity, W, D, and S represent the weight of the saturated sample, dry sample, and saturated sample suspended in water, respectively. The porosity corrected dielectric constant, using Eq. (4) provide precise values only for single phase. As mentioned above, the formation of BaWO4 might influence the dielectric constant of the specimen. The porosity of open pores of the Ba2La2ZnW2O12 ceramics that were sintered at 1400-1475 ˚C for 2 h was lowest when sintering was conducted at 1450 ˚C. The porosities, including of inner and open pores, decreased from 8.57 % to 5.12 % as sintering temperature increased from 1400 to 1475 ˚C.

Fig. 5 displays the dielectric constants and corrected dielectric constants of the $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 ˚C for 2 h. The dielectric constant of $Ba_2La_2ZnW_2O_{12}$ ceramics increased from 21.0 to 21.6 as the temperature of sintering for 2 h increased from 1400 to 1450 ˚C. It fell from 21.6 to 21.3 as the sintering temperature increased from 1450 to 1475 ˚C for 2 h. The $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1450 ˚C for 2 h had the highest dielectric constant of 21.6. Since the porosities, including of inner and open pores, decreased as sintering temperature increased from 1400 to 1475 ˚C, it is inferred that the dielectric constants of specimens increased as sintering temperature increased. However, in this study, the dielectric constants of $Ba_2La_2ZnW_2O_{12}$ ceramics decreased as the sintering temperature increased from 1450 to 1475 ˚C. This finding can be explained by the second phase. Second phase is an extrinsic factor in controlling the dielectric constant. As mentioned earlier, the appearance of second phase influences the dielectric constant. In this study, the amount of second phase increased from 1.01% to 5.65% as sintering temperature increased from 1400 to 1475 ˚C, as shown in Table 1.

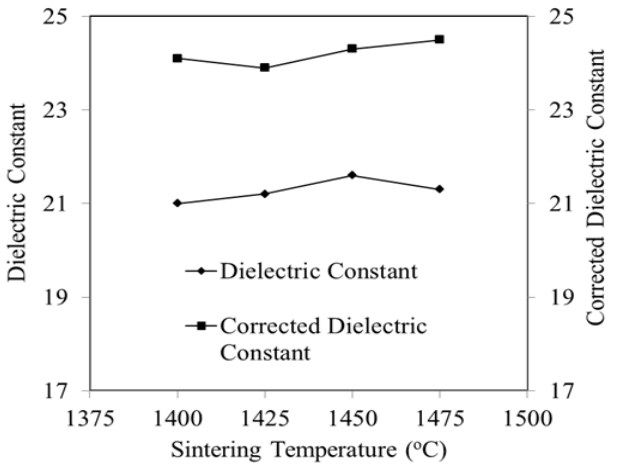

Fig. 5. Dielectric constant and corrected dielectric constant of resonant frequency (τ_f) of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h

During the second phase, a dielectric constant of 8.2 was obtained for $BaWO_4$ ceramics [9]. The dielectric constant of the composites can be calculated by the following mixture rule:

$$\ln\varepsilon_\gamma = v_1 ln\varepsilon_{\gamma 1} + v_2 ln\varepsilon_{\gamma 2} \quad (5)$$

where $\varepsilon_r$denotes the dielectric constant of the composite, v_1 and v_2 represent the volume fraction of $Ba_2La_2ZnW_2O_{12}$ and $BaWO_4$, respectively, and ε_{r1} and ε_{r2} refer to the dielectric constant of $Ba_2La_2ZnW_2O_{12}$ and $BaWO_4$, respectively. Since the amount of second phase increased significantly as sintering temperature increased from 1450 to 1475 $^{\circ}C$, the dielectric constants of specimens decreased as sintering temperature increased from 1450 to 1475 $^{\circ}C$. The corrected dielectric constant of $Ba_2La_2ZnW_2O_{12}$ ceramics can be calculated using the following equation:

$$\varepsilon_{measured} = \varepsilon_{corrected}\left(1 - \frac{3P(\varepsilon_{corrected}-1)}{2\varepsilon_{corrected}+1}\right) \quad (6)$$

where $\varepsilon_{corrected}$ and $\varepsilon_{measured}$ is the corrected and measured dielectric constants of the composite, respectively, and *P* is the fractional porosity. The corrected dielectric constant of the $Ba_2La_2ZnW_2O_{12}$ ceramics is in the range from 23.9 to 24.5 as the sintering temperature varied from 1400 to 1475 ^{o}C. No significant variation in corrected dielectric constant of $Ba_2La_2ZnW_2O_{12}$ ceramics with sintering temperature over the entire range of sintering temperatures considered herein was observed.

Fig. 6 plots the $Q \times f$ and internal strain of the $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 $^{\circ}C$ for 2 h. The $Q \times f$ of the $Ba_2La_2ZnW_2O_{12}$ ceramics increased from 19,300 to 38,900 GHz as the temperature of sintering for 2 h increased from 1400 to 1450 ^{O}C.

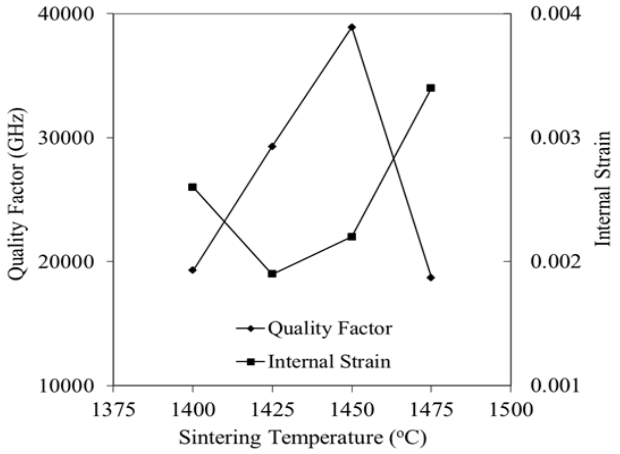

Fig. 6. $Q \times f$ and internal strain of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h

However, it declined from 38,900 to 18,700 GHz as the temperature of sintering for 2 h increased from 1450 to 1475 ^{O}C. A $Q \times f$ of 21,120 GHz was obtained for BaWO4 ceramics [9]. The $Q \times f$ of 21,120 GHz is between the $Q \times f$ of $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1400-1475 ^{O}C for 2 h, implying the presence of the second phase will not bring much deviation to the $Q \times f$ of the specimen. The $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1450 ^{O}C for 2 h had the highest $Q \times f$ of 38,900 GHz. This fact may be explained by the porosities and internal strain. Densification plays an important role in controlling the $Q \times f$. The porosities of $Ba_2La_2ZnW_2O_{12}$ ceramics, including of inner and open pores, decreased as sintering temperature increased, as shown in Fig. 4. However, the $Q \times f$ of specimens decreased significantly as sintering temperature increased from 1450 to 1475 ^{O}C. This was associated with the internal strain. The internal strain η can be calculated by following equation:

$$\beta = 2\eta\tan\theta, \quad (7)$$

where β is the full width at half maximum (FWHM) of X-ray diffraction peaks, θ is the diffraction angles. Curve fitting was used to fit the internal strain η of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h with eq. (6). The curve fittings employed were based on the least-squares method. In this method, the square of the deviation of the experimental value from the theoretical expectation was calculated while varying the fitted internal strain. The fitting process was ended at a specific value of the fitted internal strain where the deviation was minimized. The low internal strain associated with the ordering distribution of the ions, therefore, resulted in a high quality factor. There are similar examples in other microwave ceramic materials [11,12]. The internal strain of $Ba_2La_2ZnW_2O_{12}$ ceramics were lower than 0.0026 and spanned in the range from 0.0019 to 0.0026, following sintering at 1400-1450°C for 2 h. However, the internal strain of $Ba_2La_2ZnW_2O_{12}$ ceramics increased significantly as sintering temperature increased from 1450 to 1475 ˚C and, therefore, the $Q \times f$ decreased.

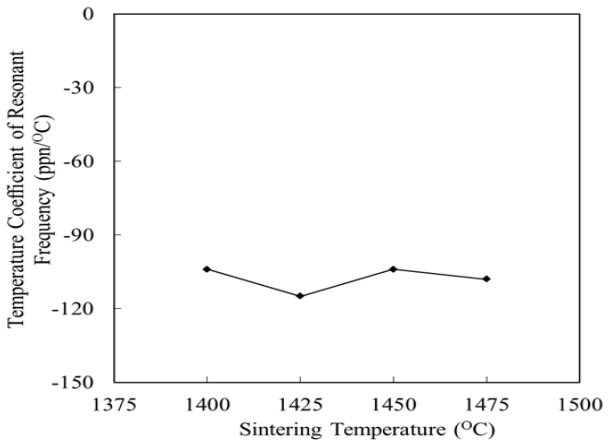

Fig. 7. τ_f of $Ba_2La_2ZnW_2O_{12}$ ceramics sintered at 1400-1475 ^{O}C for 2 h

Generally, τ_f is determined by the composition, the amount of additive, and the second phases that are present in the ceramics. The τ_f of $Ba_2La_2ZnW_2O_{12}$ ceramics ranged from -104 to -117 ppm/^{O}C as the sintering temperatures were varied. $Ba_2La_2ZnW_2O_{12}$ ceramic that was sintered at 1450 ^{O}C for 2 h had a measured τ_f of -104 ppm/^{O}C. A relatively high τ_f value of the $Ba_2La_2ZnW_2O_{12}$ ceramics precludes its immediate application potential. Efforts are underway in our laboratory to customize the τ_f value of $Ba_2La_2ZnW_2O_{12}$ ceramics. A later investigation will involve tuning the τ_f value of $Ba_2La_2ZnW_2O_{12}$ ceramics.

4. Conclusions

This study investigated how sintering temperature affect the microwave dielectric properties of $Ba_2La_2ZnW_2O_{12}$ ceramics. A second phase of $BaWO_4$ was observed in all $Ba_2La_2ZnW_2O_{12}$ ceramics. The average grain size increased with the sintering temperature. $Ba_2La_2ZnW_2O_{12}$ ceramics that were sintered at 1450 ^{O}C for 2 h had a dielectric constant of 21.6 and a $Q \times f$ of 38,900 GHz. The porosity and amount of second phase affected both the dielectric constant and $Q \times f$ of $Ba_2La_2ZnW_2O_{12}$ ceramics. Furthermore, the $Q \times f$ of $Ba_2La_2ZnW_2O_{12}$ ceramics was also depended on the internal strain.

Acknowledgments

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