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Microwave dielectric properties of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics for LTCC with near zero temperature coefficient of resonant frequency

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Abstract

The $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics have been investigated to obtain a low-temperature co-fired ceramic (LTCC). The highest quality factor (Q_f) of approximately 114,000 GHz was obtained when the ceramic with $x = 0.2$ was sintered at 950 °C for 5 h in air. The temperature coefficient of resonant frequency (τ_f) of the ceramics sintered at 1025 °C varied from −90 to 60 ppm/°C as the amount of $xBa_3(VO_4)_2$ increased, and was a near zero value in the sample obtained at $x = 0.5$ where the dielectric constant (ε_r) and the Q_f values were approximately 12 and 55,000 GHz, respectively. In order to reduce the sintering temperatures of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics, the effects of Li_2CO_3 addition as a sintering aid on the microwave dielectric properties of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics were also characterized in this study. The Li_2CO_3 addition was effective in reducing the sintering temperature without detrimental effects on the Q_f values of the ceramics. One result: the microwave dielectric properties of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ with 0.0625 wt%-doped Li_2CO_3 ceramic, which was sintered at 950 °C for 5 h in air, has a ε_r value of 13, a Q_f value of 74,000 GHz, and a τ_f value of −6 ppm/°C.

Keywords: Sintering; Dielectric properties

1. Introduction

Wireless communication technologies such as cellular phones and the global positioning system have been made rapid progress recently; microwave multilayer integrated circuits have also been widely investigated in order to reduce the size of band-pass filters and antenna duplexers. In the low temperature co-fired ceramics (LTCC), since the dielectric ceramics are co-fired with a low-loss conductor such as silver, the sintering temperature of the dielectric ceramics must be lower than the melting point of silver. Moreover, in these dielectric ceramics it is desirable to have a high quality factor (Q_f), an appropriate dielectric constant (ε_r) and a near-zero temperature coefficient of resonant frequency (τ_f).

In the MgO–V_2O_5 system, the $Mg_3(VO_4)_2$ ceramic[1] is known to be produced at relatively low temperatures; therefore, it is expected that the $Mg_3(VO_4)_2$ ceramic is one of the appropriate candidates for a LTCC material. The microwave dielectric properties of $Mg_3(VO_4)_2$ ceramic sintered at 950 °C have been reported to have a dielectric constant (ε_r) of 9, a quality factor (Q_f) of 65,000 GHz, but the improvement in the τ_f value is required for the commercial applications because the τ_f value of the ceramic is −90 ppm/°C.[2] On the other hand, in the BaO–V_2O_5 system, the $Ba_3(VO_4)_2$ ceramic which belongs to an rhombohedral phase with a space group of *R*32/*m* (No. 166) is produced at the temperatures above 700 °C.[3,4] The dielectric constant of $Ba_3(VO_4)_2$ ceramic is as low as that of $Mg_3(VO_4)_2$ ceramic as well and the Q_f and τ_f values are 62,000 GHz and 29 ppm/°C, respectively. However, the sintering temperature of $Ba_3(VO_4)_2$ ceramic is 1600 °C which is too high to use as a LTCC material.[5] When comparing the τ_f value of $Mg_3(VO_4)_2$ ceramic with that of $Ba_3(VO_4)_2$ ceramic, the $Mg_3(VO_4)_2$ ceramic has a negative value, whereas the $Ba_3(VO_4)_2$ ceramic is positive value as described above. Thus, an appropriate τ_f value which is close to 0 ppm/°C may be obtained by mixing the $Mg_3(VO_4)_2$ ceramic with $Ba_3(VO_4)_2$ ceramic. In order to tune the τ_f value of these ceramics, the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics were synthesized and then the microwave dielectric properties of these ceramics were investigated in this study. Furthermore, the effects of Li_2CO_3 addition as a sintering aid on the sintering behavior and the microwave dielectric properties of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics were also investigated to reduce the sintering temperatures of the ceramics which were lower than the melting point of silver.

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2. Experimental method

The samples with the nominal compositions of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics were prepared by using the conventional solid-state reaction method. In this study, the high-purity powders of MgO (99.9%), $BaCO_3$ (99.99%) and V_2O_5 (99.99%) were used as the starting materials. These materials were weighed according to the stoichiometric compositions of $Mg_3(VO_4)_2$ and $Ba_3(VO_4)_2$ compounds and ground for 45 min with ethanol in a mortar. After drying, the powders were calcined at 700 °C for 20 h in air and reground with ethanol. Subsequently, the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ powders were mixed to prepare the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics. The obtained powders were ground with polyvinyl alcohol as a binder and pressed at 100 MPa to form the pellets with 12 mm diameter and 7 mm thickness. These pellets were sintered at the various temperatures ranging from 950 to 1600 °C for 5 h in air.

The additions of 0.0625–1 wt% Li_2CO_3 compounds as the sintering aid into the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics were also performed to clarify the effect of Li_2CO_3 addition on the sintering temperature and the microwave dielectric properties. The Li_2CO_3-doped $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics were sintered at 950 °C for 5 h in air. The crystallization phase of the sintered samples was characterized by using X-ray powder diffraction (XRPD) with Cu Kα radiation. The microstructure of the samples was observed by means of field emission scanning electron microscopy (FE-SEM) and compositional analysis was also carried out, using energy dispersive X-ray analysis (EDX). The dielectric constant and the quality factor of the sample at microwave frequency were measured by the Hakki and Coleman method.[6] The temperature coefficient of resonant frequency of the sample was determined from the resonant frequencies obtained at the temperatures of 20 and 80 °C.

3. Results and discussion

Fig. 1 shows the XRPD patterns of the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air. At the compositions of $x = 0$ and 1, both of the $Mg_3(VO_4)_2$ and $Ba_3(VO_4)_2$ compounds were confirmed to be a single phase. In the composition range of 0.1–0.3, the formations of $Mg_3(VO_4)_2$ and $BaMg_2(VO_4)_2$ compounds were recognized, whereas the $Ba_3(VO_4)_2$ and $BaMg_2(VO_4)_2$ compounds were identified at the compositions ranging from 0.4 to 0.9. According to the equilibrium phase diagram of the $Mg_3(VO_4)_2$–$Ba_3(VO_4)_2$ system,[7] it is known that the intermediate phase of $BaMg_2(VO_4)_2$ is produced at a wide temperature range in this system.

Fig. 2 gives the bulk density of the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at various temperatures for 5 h in air. In the composition range of 0.1–0.3, the bulk densities of the samples increased with increasing the composition x from 0 to 0.2, whereas the value of the sample decrease at the compositions higher than $x = 0.2$. On the other hand, the bulk densities of the samples increased in the composition range of 0.4–0.8. From these results, the variations in the bulk densities of the samples may be attributed to the microwave dielectric properties.

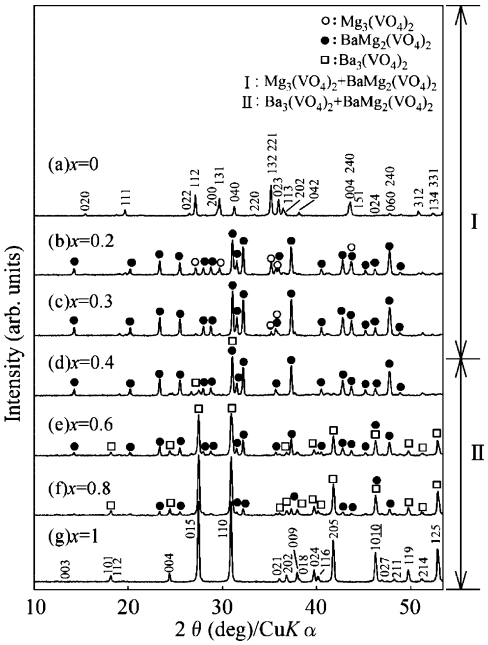

Fig. 1. XRPD patterns of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air.

The variations in the dielectric constant of the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics, which were sintered at 950, 1000 and 1025 °C for 5 h in air, are shown in Fig. 3. From these results, it is recognized that the dielectric constants of the samples depend on the compositional changes in the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics. In the composition range of 0–0.2, the dielectric constants of the ceramics increased from 6.3 to 10.5 and the value at the composition of $x = 0.2$ saturated at approximately 10.5. The dielectric constant of the ceramics at $x = 1$ is lower than those of the ceramics obtained in the composition range of 0.4–0.9 because the sintering temperatures performed in this study is too low to obtain the condensed ceramics at $x = 1$. Consequently, it was recognized that the variations in the dielectric constants of the samples were related to the bulk density.

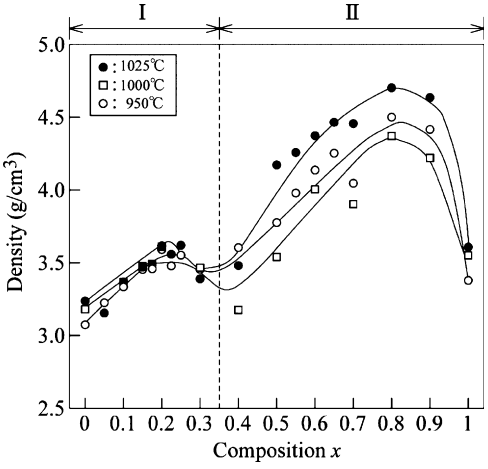

Fig. 2. Variations in bulk density of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 950, 1000 and 1025 °C for 5 h in air.

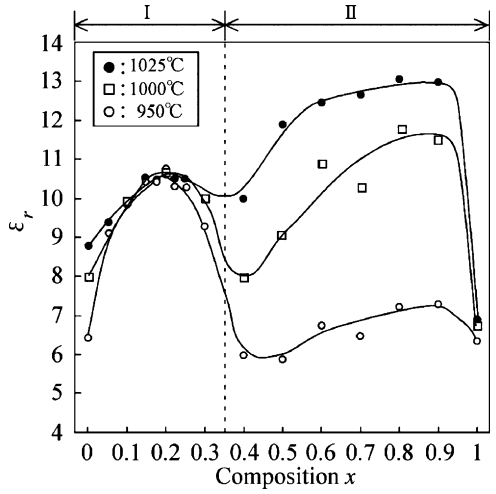

Fig. 3. Variations in dielectric constant of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 950, 1000 and 1025 °C for 5 h in air.

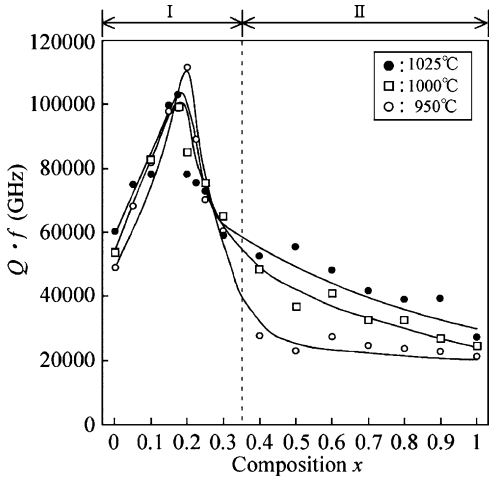

Fig. 4. Relationship between Q_f value and composition x of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics.

Fig. 4 shows the relationship between the Q_f values and sintering temperatures of the ceramics as a function of composition x. The Q_f values of the ceramics increased with increasing the composition x up to $x = 0.2$. As a result, the Q_f value of the ceramic at $x = 0.2$ sintered at 950 °C for 5 h in air is higher than 100,000 GHz and this result may be related to the formation of $BaMg_2(VO_4)_2$ compound as described above. However, the Q_f values of the ceramics decreased at the compositions higher than $x = 0.4$; these values ranged from 22,800 to 27,700 GHz in this composition range. The Q_f values of the ceramics may be caused by the morphological changes in the ceramics, since the sintering temperature of $Ba_3(VO_4)_2$ ceramic is extremely high in comparison with that of the $Mg_3(VO_4)_2$ ceramic. In order to clarify the relationship between the compositional dependences of the Q_f value and the microstructure on $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics, the morphological changes in the ceramics sintered at 950 °C for 5 h in air were investigated using FE-SEM as shown in Fig. 5. The grain growth of the samples was observed with increasing the composition, up to $x = 0.2$, and a porous microstructure was observed at the compositions above $x = 0.6$. In the binary phase diagrams of MgO–V_2O_5 and BaO–V_2O_5 systems,[1,7] it was reported that the $Mg_3(VO_4)_2$ and the $Ba_3(VO_4)_2$ compounds decomposed into the liquid phase at the temperatures of 1074 and 1610 °C, respectively. Thus, it is considered that the presence of $Ba_3(VO_4)_2$ phase in the sample exerts an influence on the sinterbility of the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics at the sintering temperature of 950 °C. Fig. 6 shows the surface FE-SEM photographs of the ceramics sintered at 1025 °C for 5 h in air. In the composition range of 0.6–1, with the ceramics obtained at 1025 °C it was observed that the grain growth and the decrease in the pore size took place in comparison with those of the samples sintered at 950 °C. From these results, the increase in the Q_f value of the ceramics may be caused by the grain growth and the formation of $BaMg_2(VO_4)_2$ compound. The temperature coefficients of resonant frequency (τ_f) of the $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics are shown in Fig. 7. The τ_f values of the ceramics changed from approximately −90 to 60 ppm/°C with increasing the composition x and a near-zero τ_f value was achieved in the composition range of 0.5–0.6. As a result, in the case of $x = 0.5$, the Q_f value of 55,000 GHz, the ε_r value of 12 and the τ_f value

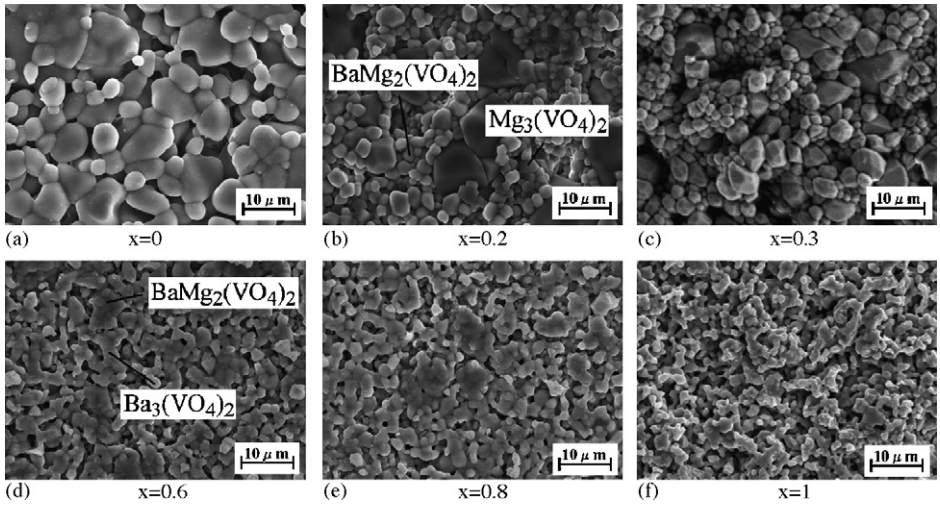

Fig. 5. Surface FE-SEM photographs of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air.

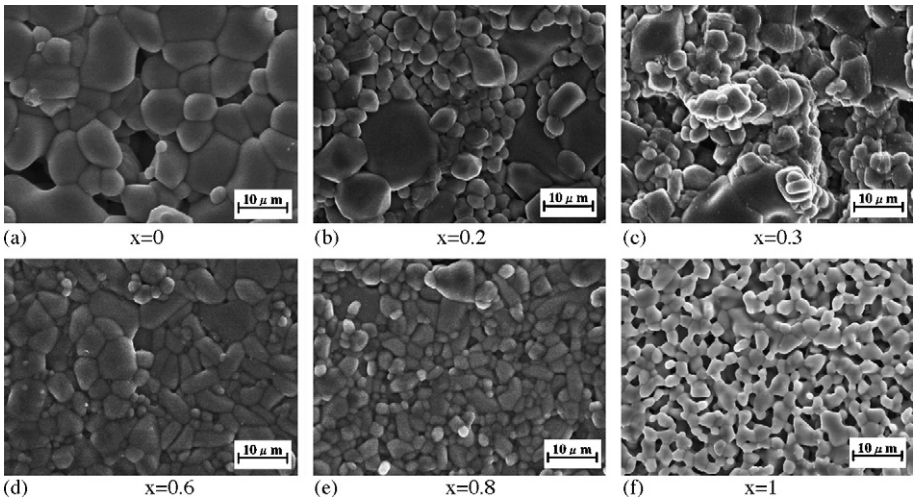

Fig. 6. Surface FE-SEM photographs of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics sintered at 1025 °C for 5 h in air.

of −13 ppm/°C were obtained when the ceramic was sintered at 1025 °C for 5 h in air. In the case of a LTCC, however, the sintering temperature of these ceramics is still too high to use silver as an electrode material and the sintering temperature of the ceramics must be lower than the melting point of silver. It was reported that the addition of sintering aids such as V_2O_5, CuO, Li_2CO_3, and K_2CO_3 was effective in lowering the sintering temperature of microwave dielectric ceramics;[8–11] therefore, the Li_2CO_3 addition into the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics was also performed to lower the sintering temperature.

The effects of Li_2CO_3 additions on the bulk density of the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic sintered at 950 °C are shown in Fig. 8; the bulk density of the samples drastically increased from 3.8 to 4.3 g/cm^3 in the amounts of Li_2CO_3 addition range from 0 to 0.0625. The bulk density of 4.3 g/cm^3 obtained at the sintering temperature of 950 °C is comparable to that of the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic sintered at 1025 °C. Thus, it was found that the 0.0625 wt% Li_2CO_3 additions were effective in improving the bulk density of the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic at the sintering temperature range of 950 °C. Furthermore, the bulk densities of the samples remained the constant value of the approximately 4.2 g/cm^3.

Fig. 9 shows the effects of Li_2CO_3 addition on the ε_r and the Q_f values of the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air. The dielectric constants of the samples increased with increased the amounts of Li_2CO_3 addi-

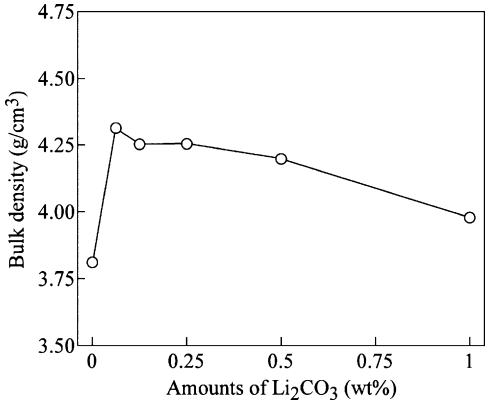

Fig. 8. Effects of Li_2CO_3 addition on bulk densities of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air.

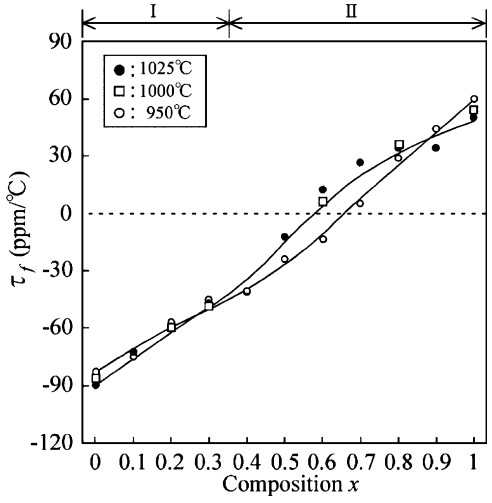

Fig. 7. Compositional dependence of temperature coefficient of resonant frequency on $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics.

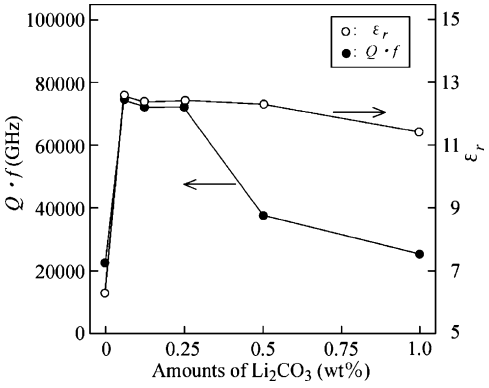

Fig. 9. Plots of dielectric constant and Q_f value of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic versus composition x.

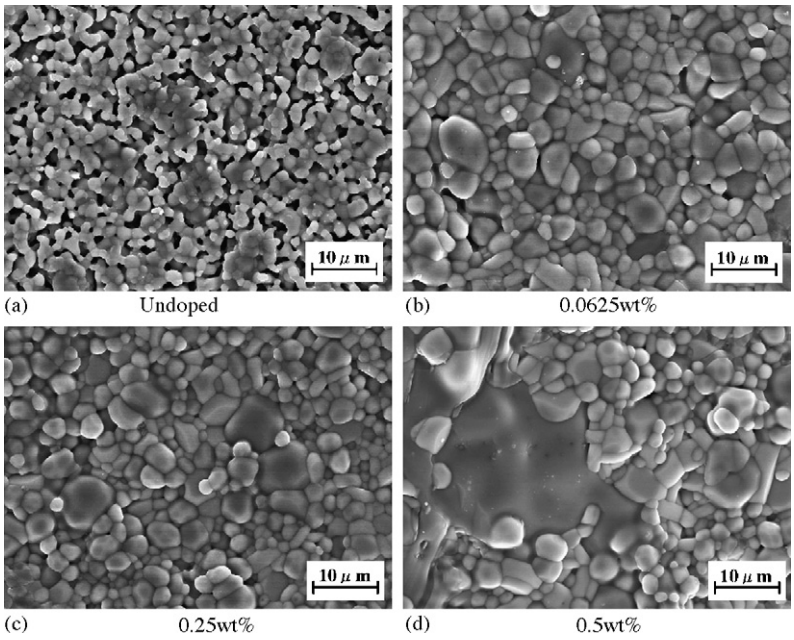

Fig. 10. Surface FE-SEM photographs of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ with different amounts of Li_2CO_3 addition ceramic sintered at 950 °C for 5 h in air.

tion and the dielectric constant of well-sintered ceramics with sintering aids saturated at the value of approximately 12.5; therefore, the dielectric constants of the samples may be attributed the bulk density, because the variation in the dielectric constant exhibited the same tendency to those of the bulk density. On the other hand, the Q_f values of the ceramics were remarkably improved by the small amounts of Li_2CO_3 additions and the maximum Q_f value of 74,400 GHz was obtained for the ceramic with 0.0625 wt% Li_2CO_3 addition. The Q_f value of a ceramic with Li_2CO_3 addition sintered at 950 °C is higher than that of the ceramic without Li_2CO_3 addition. However, the Q_f value of the ceramics decreased with increased addition of Li_2CO_3 from 0.0625 to 1.0 wt%. In order to clarify the relationships between the morphological change and the microwave dielectric properties, the microstructures of the ceramics with Li_2CO_3 additions sintered at 950 °C are characterized as shown in Fig. 10. The surface on the sintered ceramic without Li_2CO_3 addition did not show a homogeneous condensed microstructure, while the microstructures with the addition of Li_2CO_3 were observed to be dense. It is widely known that liquid phase sintering plays an important role in enhancing the densification of the ceramics at a low sintering temperature[12]; therefore, in this case, the increase in Q_f value of the ceramics by the Li_2CO_3 addition is considered to be caused by liquid phase sintering. On the other hand, the abnormal grain growth of the sample was recognized as shown in Fig. 10(d) when the 0.5 wt% Li_2CO_3 addition was performed. The morphological changes in the ceramics which depend on the amount of Li_2CO_3 addition may have an influence on the variations in the Q_f value.

Fig. 11 shows the temperature coefficient of resonant frequency of the sample sintered at 950 °C for 5 h in air. The τ_f values of the sample ranged from −23 to −6 ppm/°C; as a result, the appropriate microwave dielectric properties of $\varepsilon_r = 13$, $Q_f = 74{,}000$ GHz and $\tau_f = -6$ ppm/°C were obtained when the

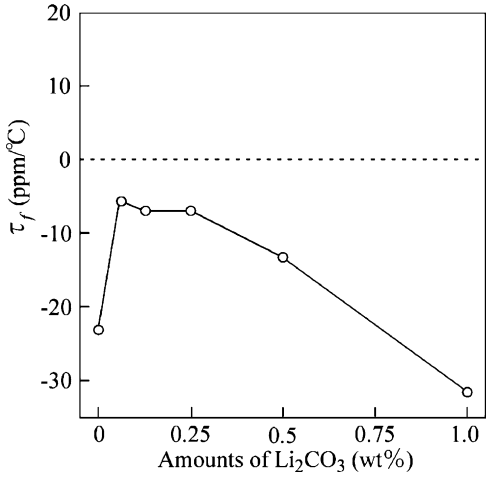

Fig. 11. Effect of Li_2CO_3 addition on temperature coefficient of resonant frequency of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramics sintered at 950 °C for 5 h in air.

$Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ with 0.0625 wt% Li_2CO_3 ceramic was sintered at the temperature of 950 °C for 5 h in air.

4. Conclusions

The microwave dielectric properties of $Mg_3(VO_4)_2$–$xBa_3(VO_4)_2$ ceramics were characterized for use as LTCC materials. At the composition of $x = 0.2$, the maximum Q_f value of 114,000 GHz with ε_r of 11 and τ_f of −58 ppm/°C was obtained when the ceramic was sintered at 950 °C for 5 h in air. Such an improvement in Q_f value which depends on the compositional changes in the ceramics may be related to the formation of intermediate phase, i.e., $BaMg_2(VO_4)_2$ ceramic. A near-zero τ_f value of the ceramic was recognized at the composition of around $x = 0.5$.

In order to reduce the sintering temperature of the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic, the effects of Li_2CO_3 addition on the sintering behavior and the microwave dielectric properties of $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic were also investigated in this study. As a result, it was found that the addition of Li_2CO_3 was effective in improving the Q_f value and lowering the sintering temperature of the ceramics without any detrimental effect on the ε_r and τ_f values. Thus, the $Mg_3(VO_4)_2$–$0.5Ba_3(VO_4)_2$ ceramic with 0.0625 wt% Li_2CO_3 addition exhibited the appropriate microwave dielectric properties of $\varepsilon_r = 12.6$, $Q_f = 74{,}434$ GHz and $\tau_f = -5.8$ ppm/°C when the ceramic was sintered at 950 °C for 5 h in air.

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