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Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2$ ceramic

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Abstract

In order to develop a new low-temperature co-fired ceramics (LTCC), the microwave dielectric properties and microstructure of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics were investigated. The grain growth of $Mg_3(VO_4)_2$ ceramic was observed as the sintering temperature was increased from 750 to 1050 °C; the maximum $Q\cdot f$ value of 65,440 GHz was obtained at the sintering temperature of 1050 °C. At a sintering temperature of 1075 °C, the $Mg_3(VO_4)_2$ ceramic decomposed to form the MgO and liquid phases; the $Q\cdot f$ value of the sample decreased. As for the Co substitution for Mg, the XRPD patterns of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics showed a single phase over the whole composition range; the individual curves indicated the maximum values for density which gradually converge as the sintering temperature is increased but the values shift toward the lower sintering temperatures with Co substitution for Mg. As a result, a $Q\cdot f$ value of 78,906 GHz with a dielectric constant of 9.5 was obtained at $x = 2$ when the sample was sintered at 900 °C for 5 h in air, whereas the temperature coefficient was −94.5 ppm/°C.

Keywords: Powders-solid state reaction; X-ray method; MgO; Electron microscopy

1. Introduction

The rapid development in microwave telecommunication system has been creating a high demand for multilayer microwave devices in order to reduce the size of band-pass filters and antenna duplexers. Thus, it is necessary to lower the sintering temperature of the dielectric ceramics because the dielectric ceramics and electrode metals with low resistivity such as Ag and Cu should be co-fired in the case of multilayer microwave devices. In order to reduce the sintering temperature of dielectric ceramics, there are several methods commonly explored: (1) the addition of low melting point compounds such as Bi_2O_3, B_2O_3 and V_2O_5,[1–3] (2) the chemical processing and smaller particle size of starting materials by the sol–gel and coprecipitation methods, and (3) a study of new series in the low-temperature co-fired ceramics (LTCC) materials. The first method is widely used to reduce the sintering temperature of commercially developed dielectric ceramics; however, in many cases, the additions of Bi_2O_3, B_2O_3 and V_2O_5 to the dielectric ceramics produce a significant deterioration in $Q\cdot f$ values. In the case of second method, i.e., sol–gel and coprecipitation methods, these chemical techniques require the flexible processing in order to synthesize the dielectric ceramics. Consequently, the third method is the development of new dielectric ceramics with low sintering temperature. In the MgO–V_2O_5 system, it is reported that the $Mg_3(VO_4)_2$ compound decomposes into the $Mg_3(VO_4)_2$ compound and liquid phase at the temperature of 980 °C.[4] On the other hand, in the case of $Co_3(VO_4)_2$ compound, the decomposition temperature of $Co_3(VO_4)_2$ compound into $Co_3(VO_4)_2$ compound and liquid phase is known to be approximately 850 °C.[5] Therefore, it is considered that the $Mg_3(VO_4)_2$ compound is an appropriate candidate as a LTCC material; the Co substitution for Mg may be effective in reducing the sintering temperature of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics because of the differences in the melting point between the $Mg_3(VO_4)_2$ and $Co_3(VO_4)_2$ ceramics. Therefore,

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this paper focused on the evaluation of microwave dielectric properties and microstructure for the low-temperature sintered $Mg_3(VO_4)_2$ ceramic. Then, the effects of the Co substitution for Mg on the microwave dielectric properties of the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramic were also investigated.

2. Experimental method

For the preparation of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics, the starting materials were MgO, CoO and V_2O_5 powders with 99.9% purity and the samples were prepared by using the conventional solid-state reaction method. In this study, these powders were mixed with ethanol for 45 min in a mortar and then calcined at 700 °C for 20 h in air. The obtained powders were ground with an organic binder (polyvinyl alcohol) and uniaxially pressed into the pellets of 12 mm in diameter and 7 mm in thickness under a pressure of 100 MPa. These pellets were sintered in the temperature range of 750–1075 °C for 5–50 h in air. The sintered samples were identified by the X-ray powder diffraction (XRPD; MiniFlex, Rigaku); the microstructure of the samples was observed by means of a field emission electron scanning microscopy (FE-SEM; JSM 6330-F, JEOL). The bulk densities of the samples were determined by the Archimedes method. The microwave dielectric properties were measured by the Hakki and Coleman method;[6] the temperature coefficients of resonant frequency (τ_f) were measured at the two temperatures (20 and 80 °C).

3. Results and discussion

The bulk densities of $Mg_3(VO_4)_2$ ceramics sintered at various temperatures for 5 h in air are shown in Fig. 1. The bulk densities of the samples increased with increasing the sintering temperatures from 750 to 1050 °C, and then these values were saturated at the sintering temperatures higher than 1050 °C. This result indicates that the $Mg_3(VO_4)_2$ ceramic is densified at the temperature of 1050 °C. The sintering temperature dependence of dielectric constant (ε_r) is also shown in Fig. 1. The ε_r values of the samples range from 4.4 to 9.4 depending on the sintering temperatures. In general, in the LTCC materials, it is well known the variation in the dielectric constant is strongly affected by the improvement in the bulk density;[7] the variations in the dielectric constant showed the similar tendency to those of bulk density. Thus, it is considered that the improvement in the dielectric constant, which depends on the sintering temperature, is due to the bulk density of the samples. The influences of sintering temperatures on the quality factor ($Q\cdot f$) of $Mg_3(VO_4)_2$ ceramics sintered for 5 h in air are shown in Fig. 2. A significant variations in $Q\cdot f$ values which arisen from the variations in the sintering temperature was observed in the sintering temperature range of 750–1050 °C, and then a maximum $Q\cdot f$ value of 65,440 GHz was obtained when the sample was sintered at 1050 °C. Yang et al.[8] reported that the improvement in bulk density and grain growth of the dielectric ceramics play an important role in improving the $Q\cdot f$ value. Therefore, the improvement in $Q\cdot f$ value of $Mg_3(VO_4)_2$ compound in the sintering temperature range of 750–1050 °C may relate with the morphological changes in the samples. At the sintering temperature of 1075 °C, however, the $Q\cdot f$ value of $Mg_3(VO_4)_2$ compound decreased in comparison with that of the sample sintered at 1050 °C. According to the binary phase diagram of $MgO–V_2O_5$ system reported by Kerby and Wilson,[4] it is known that the $Mg_3(VO_4)_2$ compound decomposes to form a liquid phase at a temperature of approximately 1074 °C; it suggests that the decrease in $Q\cdot f$ value at the sintering temperature of 1075 °C relates with the presence of liquid phase because Weng and Huang[7] reported that the $Q\cdot f$ values of low-temperature sintered $Ba_2Ti_9O_{20}$ by the addition of $PbO–B_2O_3–SiO_2$ decreased with increasing the amount of liquid phase. Thus, in order to clarify the relationship between microstructure and microwave dielectric properties of $Mg_3(VO_4)_2$ compound, the microstructure of the samples sintered at the various sintering temperatures was investigated; the results are shown in Fig. 3. With increasing the sintering temperature from 750 to 1050 °C, the grain growth of the samples was recognized. Thus, the improvements in bulk density, dielectric constant and $Q\cdot f$ value of $Mg_3(VO_4)_2$ compound in the sintering temperature range of

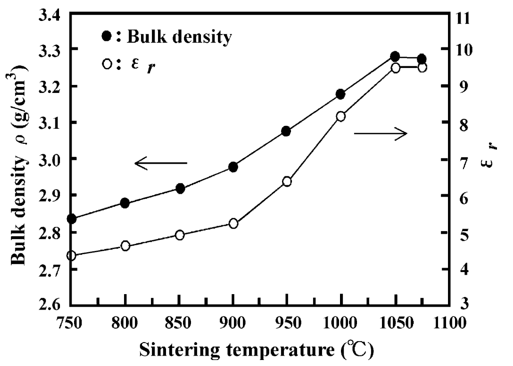


Fig. 1. Variations of bulk density and dielectric constant of $Mg_3(VO_4)_2$ ceramic sintered for 5 h in air as a function of sintering temperature.

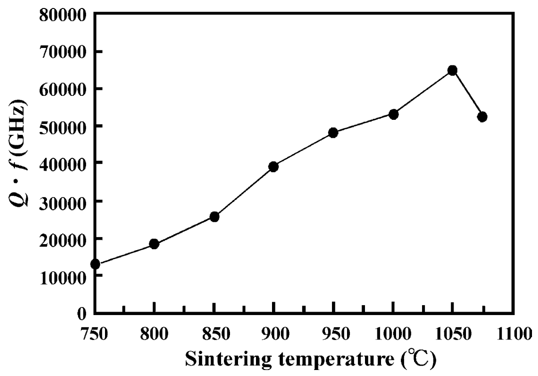
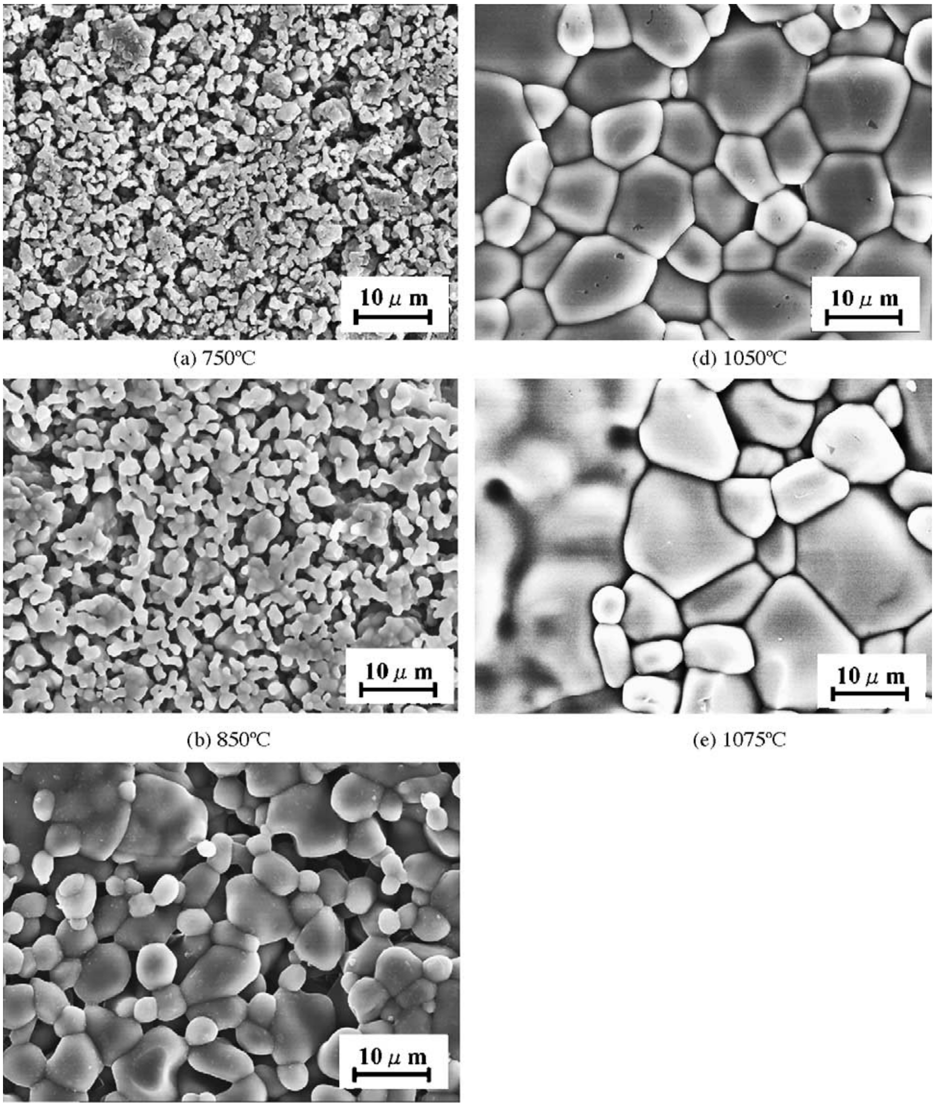


Fig. 2. Relationship between $Q\cdot f$ value and sintering temperature of $Mg_3(VO_4)_2$ ceramic sintered for 5 h in air.



(a) 750℃ (d) 1050℃

(b) 850℃ (e) 1075℃

(c) 950℃

Fig. 3. Surface FE-SEM photographs of $Mg_3(VO_4)_2$ ceramics sintered at (a) 750 °C, (b) 850 °C, (c) 950 °C, (d) 1050 °C and (e) 1075 °C for 5 h in air.

750–1050 °C are attributed to the grain growth of the samples. However, the presence of liquid phase was observed when the samples was sintered at 1075 °C as marked in Fig. 3e; this result was consistent with the binary phase diagram of $MgO–V_2O_5$ system.[4] Therefore, it is considered that the decomposition of $Mg_3(VO_4)_2$ compound into the liquid phase has a detrimental effect on the $Q{\cdot}f$ value; the microstructure-microwave dielectric property relations in this system agreed with those of LTCC materials by liquid phase sintering.[7–9] As for the relationship between the sintering temperature and τ_f of $Mg_3(VO_4)_2$ ceramic, the τ_f value of the samples decreased from −62.4 to −91.9 ppm/°C as shown in Fig. 4; the improvement in τ_f values is required for the microwave application. From these results, the $Mg_3(VO_4)_2$ ceramic is considered to be one of the attractive candidates as a new

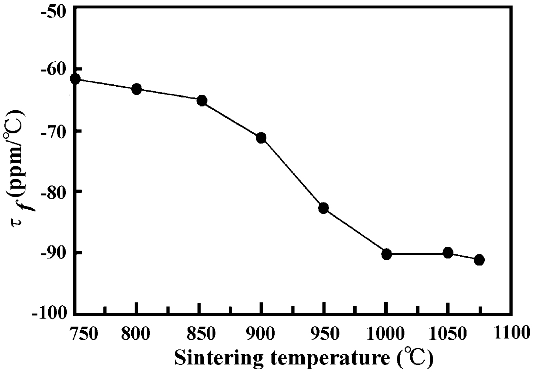


Fig. 4. Influence of sintering temperature on temperature coefficient of resonant frequency of $Mg_3(VO_4)_2$ ceramic.

Table 1
Microwave dielectric properties of $Mg_3(VO_4)_2$ ceramics sintered for 5, 10, 25 and 50 h at 950 °C in air

Sintering time (h)	ρ (g/cm^3)	ε_r	$Q\cdot f$ (GHz)	τ_f (ppm/°C)
5	3.08	6.4	48800	−83.3
10	3.20	7.9	52977	−84.3
25	3.31	8.8	61948	−93.2
50	3.34	9.1	64142	−93.2

ρ: bulk density, ε_r: dielectric constant, $Q\cdot f$: quality factor, τ_f: temperature coefficient of resonant frequency.

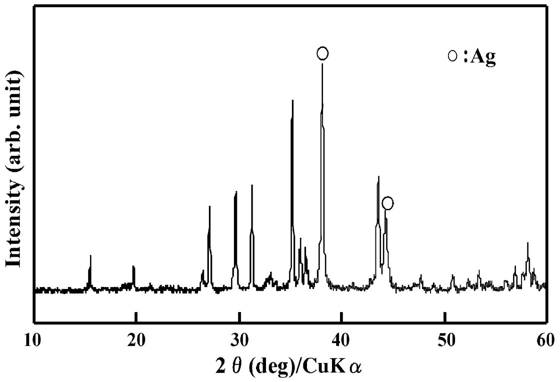


Fig. 5. XRPD patterns of the mixture $Mg_3(VO_4)_2$ and Ag heat-treated at 920 °C for 1 h in air.

LTCC material because of its low sintering temperature and high $Q\cdot f$ value.

For the $Mg_3(VO_4)_2$ ceramic, the optimum sintering temperature has been found to be 1050 °C as mentioned above; however, the sintering temperature is still too high to use silver as an electrode in the case of LTCC. Thus, in this study, in order to obtain the high $Q\cdot f$ value at a sintering temperature lower than the melting point of silver, the sintering time dependence of microwave dielectric properties of $Mg_3(VO_4)_2$ ceramic sintered at 950 °C in air was also investigated. It was generally known that the variation in the sintering time was effective in improving the $Q\cdot f$ value which is related to the grain growth of the samples.[10] Table 1 shows the microwave dielectric properties of $Mg_3(VO_4)_2$ ceramics sintered for 5, 10, 25 and 50 h at 950 °C in air. The bulk densities and ε_r of the samples ranged from 2.83 to 3.34 g/cm^3 and 4.4 to 9.1, respectively; these values increased when increasing the sintering time. Moreover, the sintering time dependence of $Q\cdot f$ value was also recognized; the $Q\cdot f$ value of 64,142 GHz, which was comparable to that of the $Mg_3(VO_4)_2$ ceramic sintered at 1050 °C for 5 h, was obtained when the sample was sintered at 950 °C for 50 h. It is considered that the grain growth of the samples caused by the increase in the sintering time improves the ε_r and $Q\cdot f$ values. Thus, by increasing in the sintering time from 5 to 50 h, the $Mg_3(VO_4)_2$ ceramic was densified at the temperature of 950 °C which is lower than the melting point of silver. In the case of the multilayer microwave dielectric devices, the LTCC material and silver should be co-fired; the chemical compativility with silver is required. In order to evaluate the chemical compativility of $Mg_3(VO_4)_2$ ceramic with silver, mixtures of $Mg_3(VO_4)_2$ ceramic and Ag powders were heat-treated at 920 °C for 1 h in air; the XRPD pattern of the mixtures was shown in Fig. 5. Since the XRPD pattern of the mixtures did not show the formation of secondary phase, it is considered that the $Mg_3(VO_4)_2$ compound has a chemical compatibility with silver.

In this study, the effect of Co substitution for Mg on the microwave dielectric properties of the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics was also investigated because it was reported that the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramic at $x = 3$, i.e., $Co_3(VO_4)_2$ ceramic, was the same crystal structure of $Mg_3(VO_4)_2$ ceramic.[11] Fig. 6 shows the XRPD patterns of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air. From the XRPD patterns, any secondary phase was not detected over the whole composition range.

The relationship of the bulk density, composition x and sintering temperature of the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics is shown in Fig. 7. In the cases of $x = 2$ and 3, the saturated values of bulk densities were obtained at the sintering temperatures of 850 °C for $x = 3$ and 900 °C for $x = 2$, respectively; the sintering temperature of the samples was lowered by the Co substitution for Mg. Brisi[5] reported the detail on the binary phase diagram of CoO–V_2O_5 system; in the diagram, it is known that the $Co_3(VO_4)_2$ ceramic decomposes to form the liquid phase and $Co_3(VO_4)_2$ ceramic at the temperature of approximately 850 °C. Then, at the temperatures above 1000 °C, the $Co_3(VO_4)_2$ ceramic decomposes to form the CoO and liquid phases. Therefore, the densification of $Co_3(VO_4)_2$ ceramics by the Co substitution for Mg may be due to the presence of

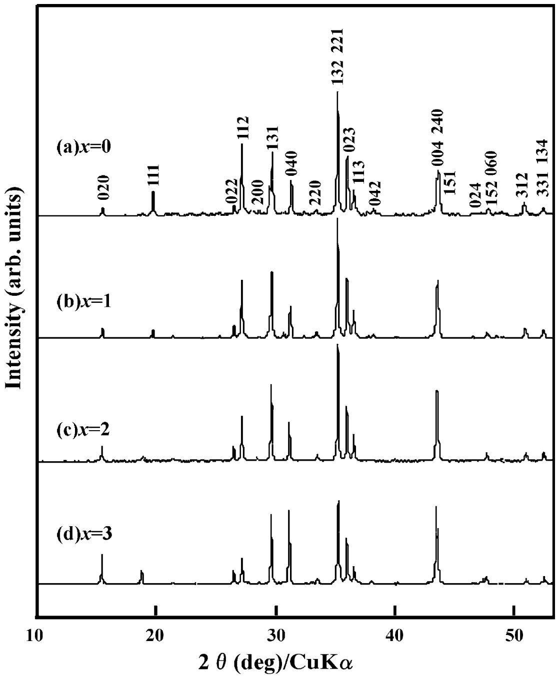


Fig. 6. XRPD patterns of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air.

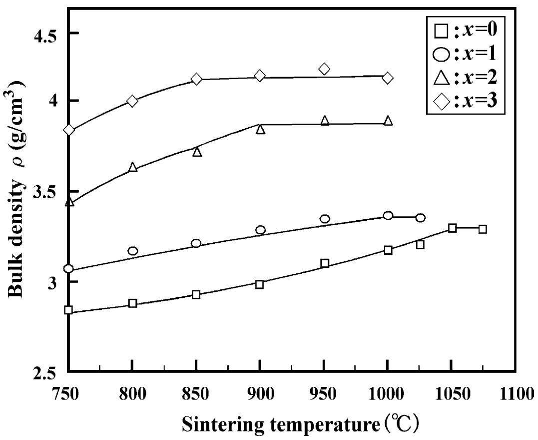


Fig. 7. Sintering temperature dependence of bulk density of ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics.

a liquid phase; the formation of a liquid phase plays an important role in improving the bulk density at the low sintering temperature. The effects of Co substitution for Mg on the ε_r and $Q\cdot f$ values of the ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics sintered at the various temperatures are shown in Fig. 8. The same tendency was observed with the dielectric constant and bulk density. Sintering temperature dependence of the $Q\cdot f$ values is shown in Fig. 8b. The maximum $Q\cdot f$ value is effected by varying the chemical composition of ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics when the sintering temperature is increased. Thus, it is found that the Co substitution for Mg is effective in improving the $Q\cdot f$ value and reducing the sintering temperature of ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics; as a result, in the cases of

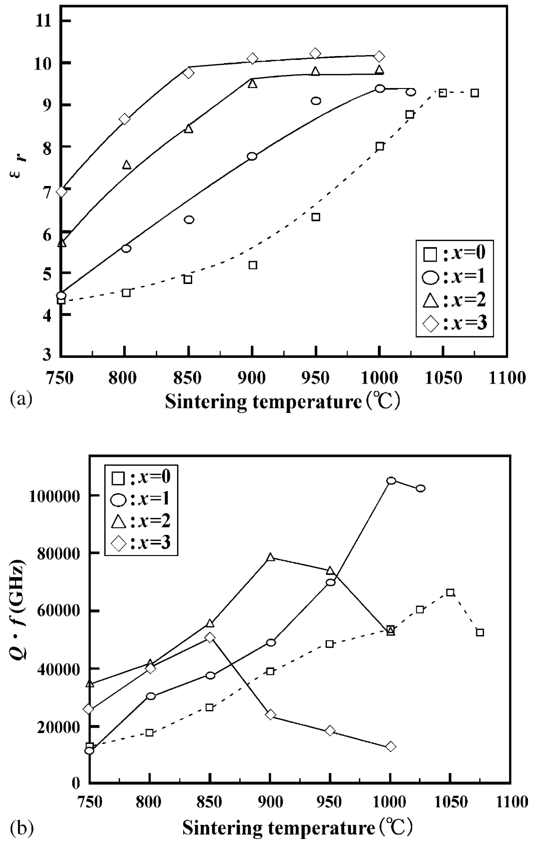
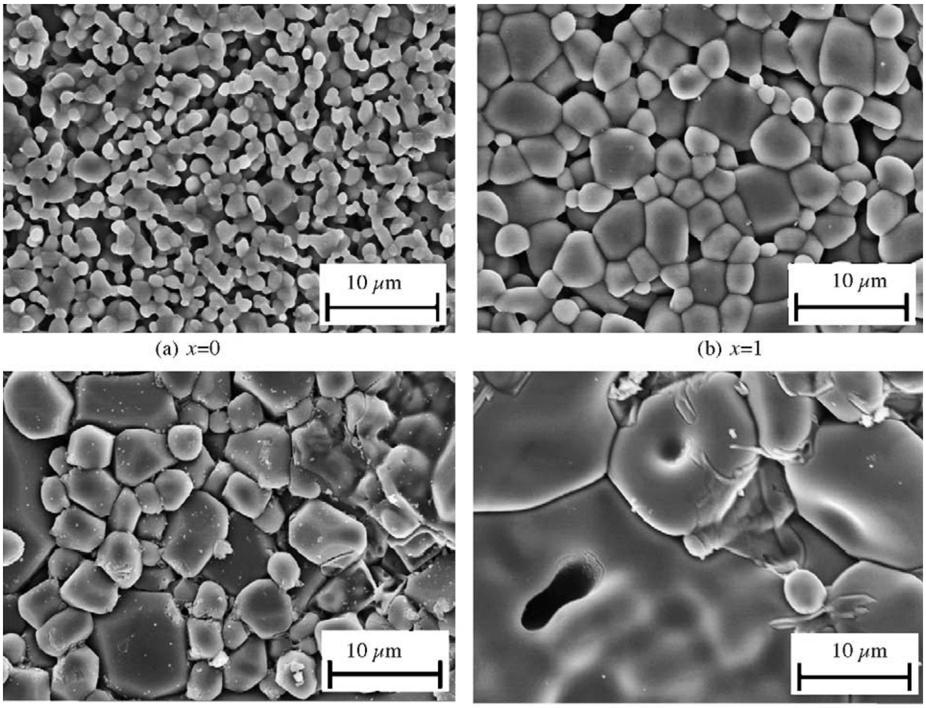


Fig. 8. Effect of Co substitution for Mg on (a) dielectric constant and (b) $Q\cdot f$ value of ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics.



(a) x=0

(b) x=1

(c) x=2

(d) x=3

Fig. 9. Surface FE-SEM photographs of ($Mg_{3-x}Co_x$)(VO_4)$_2$ ceramics sintered at 900 °C for 2 h after quenching in liquid nitrogen.

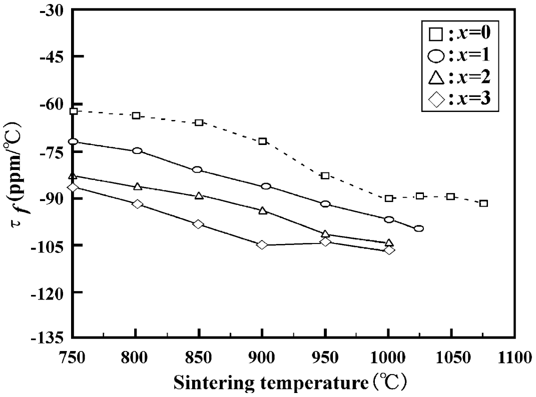


Fig. 10. Sintering temperature dependence on τ_f values of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics.

$x = 2$ and 3, the individual highest $Q{\cdot}f$ values were obtained at the sintering temperatures of 900 and 850 °C, respectively, which are lower than the melting point of silver. Although the improvement in $Q{\cdot}f$ value of the samples was recognized by the Co substitution for Mg, the variations in $Q{\cdot}f$ values seem to strongly depend on the composition x; it is considered that the morphological changes in the samples exert an influence on the $Q{\cdot}f$ values. Thus, in this study, the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics were sintered at 900 °C; the microstructures of the samples after quenching in liquid nitrogen were investigated in terms of FE-SEM as shown in Fig. 9. When comparing the microstructure of the samples at $x = 1$ with that of the samples at $x = 0$, the grain growth of the samples at $x = 1$ was recognized. Moreover, comparing the grain size of the samples at $x = 2$ with that of the samples at $x = 1$, the grain size of the samples at $x = 2$ is larger than that of the samples at $x = 1$. Thus, the increase in the $Q{\cdot}f$ value of the samples at 900 °C caused by the Co substitution for Mg is attributed to the grain growth of the samples. As for the microstructure of the sample at $x = 3$, the presence of the liquid phase is predominant because the $Co_3(VO_4)_2$ ceramic decomposed into a liquid phase and $Co_3(VO_4)_2$ ceramic in the temperature range of 850–1000 °C.[5] Thus, the $Q{\cdot}f$ value at $x = 3$ in comparison with those at $x = 0$, 1 and 2 may be related to the presence of liquid phase. Fig. 10 shows the temperature coefficient of resonant frequency of the samples sintered at the temperature range of 750–1075 °C. The τ_f values of the samples decreased with increasing the sintering temperatures; these values ranged from −60 to −105 ppm/°C. Thus, the additional improvement in τ_f is required for the commercial applications.

4. Conclusions

The sintering temperature dependence of microwave dielectric properties of the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics was investigated in order to develop a new LTCC material. A $Q{\cdot}f$ value of 64,142 GHz with a dielectric constant of 9.1 and a τ_f value of −93.2 ppm/°C was obtained for the $Mg_3(VO_4)_2$ ceramic after sintering at 950 °C for 50 h; any chemical reaction between $Mg_3(VO_4)_2$ ceramic and Ag was not recognized from the XRPD pattern. Moreover, by the Co substitution for Mg, the sintering temperatures of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics were reduced from 1050 to 850 °C because of the formation of a liquid phase in the $CoO–V_2O_5$ system. As a result, when the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramic with $x = 2$ was sintered at 900 °C for 5 h, the $Q{\cdot}f$ value of 78,906 GHz which was comparable to that of the $Mg_3(VO_4)_2$ ceramic sintered at 1050 °C for 5 h was obtained; it was found that the Co substitution for Mg in the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics exerts an influence on the variations in $Q{\cdot}f$ and τ_f values. From the evaluation of microwave dielectric properties, the $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics are considered to be one of the appropriate candidates as a LTCC material.

References

1. Kagata, H., Inoue, T., Kato, J. and Kameyama, I., Low-fire bismuth-based dielectric ceramics for microwave use. *Jpn. J. Appl. Phys.*, 1992, **31**, 3152–3155.
2. Kim, H. T., Kim, S. H., Nahm, S. and Byun, J. D. J., Low-temperature sintering and microwave dielectric properties of zinc metatitanate–rutile mixture using boron. *Am. Ceram. Soc.*, 1999, **82**, 3043–3048.
3. Tzou, W. C., Yang, C. F., Chen, Y. C. and Cheng, P. S., Improvements in the sintering and microwave properties of $BiNbO_4$ microwave ceramics by V_2O_5 addition. *J. Eur. Ceram. Soc.*, 2000, **20**, 991–996.
4. Kerby, R. C. and Wilson, J. R., Solid–liquid phase equilibriums for the ternary systems vanadium(V) oxide–sodium oxide–iron(III) oxide, vanadium(V) oxide–sodium oxide–chromium(III) oxide, and vanadium(V) oxide–sodium oxide–magnesium oxide. *Can. J. Chem.*, 1973, **51**(7), 1032–1040.
5. Brisi, C., The systems nickel oxide–vanadic anhydride and cobaltous oxide–vanadic anhydride. *Ann. Chim. (Rome)*, 1957, **47**(7–8), 806–816.
6. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive in the millimeter range. *IRE Trans: Microwave Theory Tech.*, 1960, **MTT-8**, 402–410.
7. Weng, M. H. and Huang, C. L., Single phase $Ba_2Ti_9O_{20}$ microwave dielectric ceramics prepared by low temperature liquid phase sintering. *Jpn. J. Appl. Phys.*, 2000, **39**(Part 1 6A), 3528–3529.
8. Yang, J. I., Nahm, S., Choi, C. H., Lee, H. J. and Park, H. M., Microstructure and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with ZrO_2 addition. *J. Am. Ceram. Soc.*, 2002, **85**(1), 165–168.
9. Weng, M. H. and Huang, C. L., Liquid phase sintering of $(Zr,Sn)TiO_4$ microwave dielectric ceramics. *Mater. Res. Bull.*, 2000, **35**, 1881–1888.
10. Matsumoto, H., Tamura, H. and Wakino, K., $Ba(Mg,Ta)O_3–BaSnO_3$ high-Q dielectric resonator. *Jpn. J. Appl. Phys.*, 1991, **30**(9B), 2347–2349.
11. Sauerbrei, E. E., Fraggiani, R. and Calvo, C., Refinement of the crystal structures of cobalt vanadate $(Co_3V_2O_8)$ and nickel $(Ni_3V_2O_8)$. *Acta Crystallogr.*, 1973, **B29**, 2304–2306.