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 ; the maximum $Q \cdot f$ value of 65440 GHz was obtained at the sintering temperature of 1050 . At a sintering temperature of 1075 , 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 78906 GHz with a dielectric constant of 9.5 was obtained at $x = 2$ when the sample was sintered at 900 for 5h in air, whereas the temperature coefficient was -94.5 ppm/ .

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

Introduction

The rapid development in microwave telecommunication system has been creating a high demand for the 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 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 f values. The second method includes a problem, which is the high cost of individual processing. Consequently, the third method is the development of new dielectric ceramics with low sintering temperature. In MgO-V_2O_5 system, the $Mg_3(VO_4)_2$ compound was partially melted at 980 [4)], whereas the partial melting of $Co_3(VO_4)_2$ compound took place at the temperature of approximately 850 [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, 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.

Experimental

For the preparation of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics, the starting materials were reagent-grade MgO, CoO and V_2O_5 ($\geq$99.9) powders 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 for 20h in air. The obtained powders were ground with an organic binder (polyvinyl alcohol) and uniaxially pressed into the pellets of 12mm in diameter and 7mm in thickness under a pressure of 100 MPa. These pellets were sintered at the temperature range of 750°- 1075 for 5-50h in air. The sintered samples were identified by the X-ray powder diffraction (XRPD); the microstructure of the samples was observed by means of a field emission electron scanning microscopy (FE-SEM). 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).

Results and discussion

The bulk densities of $Mg_3(VO_4)_2$ ceramics sintered at various temperatures for 5h in air are shown in Fig.1. The bulk densities of the samples increased with increasing the sintering temperatures from 750°to 1050 , and then these values were saturated at the sintering temperatures higher than 1050 . This result indicates that the $Mg_3(VO_4)_2$ ceramic is densified at the temperature of 1050 . 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. Although the variations in dielectric constant of the ceramics exhibited a similar tendency to those of bulk density, the increase in the dielectric constant is related to the improvement in the bulk density which arises from the increase in the sintering temperatures. The influences of sintering temperatures on the quality factor (Q f) of $Mg_3(VO_4)_2$ ceramics sintered for 5h in air are shown in Fig.2. A near-liner dependence of Q f values on sintering temperature is observed in the sintering temperature range of 750°- 1050 ; the maximum Q f value of 65440 GHz was obtained at 1050 . At the sintering temperatures above 1050 , however, the Q f value of the sample was decreased in comparison with that of the sample sintered at 1050 , though the bulk density of the sample sintered at 1075 was similar to that of the sample sintered at 1050 . According to the binary phase diagram of $MgO-V_2O_5$ system reported by Kerby et $al.$[4], it is known that the $Mg_3(VO_4)_2$ ceramic decompose to form a liquid phase at the temperature of approximately 1074 ; the decrease in the Q f value as described above may be related to the decomposition of the $Mg_3(VO_4)_2$ ceramic. Thus, in order to clarify the relationship between the morphological changes in the samples, which depend on the sintering temperature and microwave dielectric properties, the microstructure of the samples was investigated in terms of FE-SEM; the results are shown in Fig.3. From FE-SEM observation, it can be seen that the grain growth of the samples takes place with increasing the sintering temperature up to 1050 , and then the improvements in the bulk density, dielectric constant and Q f values of the samples in the sintering temperature range of 750°- 1050 are considered to be caused by the grain growth of the samples. However, the presence of a liquid phase was observed

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when the sample was sintered at 1075   as shown in Fig.3(e); this result was consistent with the binary phase diagram of MgO-V_2O_5 system[4]. Therefore, it is considered that the decomposition of $Mg_3(VO_4)_2$ ceramic into the liquid phase has a detrimental effect on the Q f value in this system. 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/   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 LTCC material because of its low sintering temperature and high Q f value.

In the $Mg_3(VO_4)_2$ ceramic, the optimum sintering temperature was found to be 1050   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 f value at the 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   in air was also investigated. Because it was generally known that the variation in the sintering time was effective in improving the Q f value which is related to the morphological changes in the samples. Table 1 shows the microwave dielectric properties of $Mg_3(VO_4)_2$ ceramics sintered for 5, 10, 25 and 50h at 950   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 with increasing the sintering time. Moreover, the sintering time dependence of Q f value was also recognized; the Q f value of 64142 GHz, which was comparable to that of the $Mg_3(VO_4)_2$ ceramic sintered at 1050   for 5h, was obtained when the sample was sintered at 950   for 50h. It is considered that the grain growth of the samples caused by the increase in the sintering time improves the ε_r and Q f values. Thus, by increasing in the sintering time from 5 to 50h, the $Mg_3(VO_4)_2$ ceramic was densified at the temperature of 950   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, the mixtures of $Mg_3(VO_4)_2$ ceramic and Ag powders were heat-treated at 920   for 1h 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, in this material, silver can be used as

an electrode material.

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 compound of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramic at $x = 3$, i.e., $Co_3(VO_4)_2$ ceramic, has the same crystal structure as that of $Mg_3(VO_4)_2$ ceramic[7]. Figure 6 shows the XRPD patterns of $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics sintered at 750 for 5h 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. The bulk density of the sample increased with increasing the sintering temperature; these values reached a saturation value at a certain temperature that depended on the composition x. Especially, in the cases of $x = 2$ and 3, the saturated values of bulk densities were obtained at the sintering temperatures of 850 for $x = 3$ and 900 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 . Then, at the temperatures above 1000 , 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 is due to the presence of 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 Fig8.(b). 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 $x = 2$ and 3, the individual highest $Q \cdot f$ values were obtained at the sintering temperatures of 900°and 850 , 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 ; 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, the grain size of the samples at $x = 2$ is larger than that of the samples at $x = 1$, though the partial melting of the samples is observed at $x = 2$. Thus, the increase in the $Q \cdot f$ value of the samples at 900 caused by the Co substitution for Mg is substantially due to the densification 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 [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. Figure 10 shows the temperature coefficient of resonant frequency of the samples sintered at the temperature range of 750°- 1075 . The τ_f values of the samples decreased with increasing the sintering temperatures; these values ranged from -60 to -105 ppm/ . Thus, the additional improvement in τ_f is required for the commercial applications.

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 64142 GHz with a dielectric constant of 9.1 and a τ_f value of -93.2 ppm/ was obtained for the $Mg_3(VO_4)_2$ ceramic after sintering at 950 for 50h; 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 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 for 5h, the $Q \cdot f$ value of 78906 GHz which was comparable to that of the $Mg_3(VO_4)_2$ ceramic sintered at 1050 for 5h was obtained; it was found that the morphological changes in $(Mg_{3-x}Co_x)(VO_4)_2$ ceramics by the Co substitution for Mg exert an influence on the

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variations in Q 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,** 3043-48.

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 ( ) Oxide-Sodium Oxide-Iiron ( ) Oxide, Vanadium ( ) Oxide-Sodium Oxide-Chromium ( ) Oxide, and Vanadium ( ) 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. 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.

Figure Captions

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

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

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

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

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

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

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

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

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

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

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Fig.1

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Fig.2

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(a)750℃

(d)1050℃

(b)850℃

(e)1075℃

(c)950℃

Fig.3

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Fig.4

○ :Ag

Intensity (arb. unit)

2 θ (deg)/Cu$K\alpha$

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Fig.5

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Fig.6

Fig.7

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(a)

(b)

Fig.8

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(a) *x*=0   **(b)** *x*=1

(c) *x*=2   **(d)** *x*=3

Fig.9

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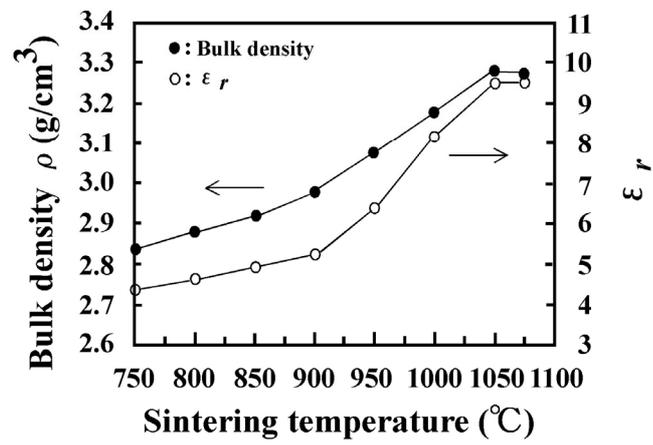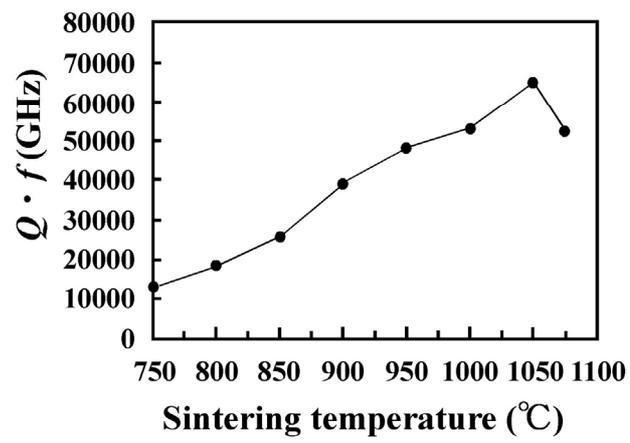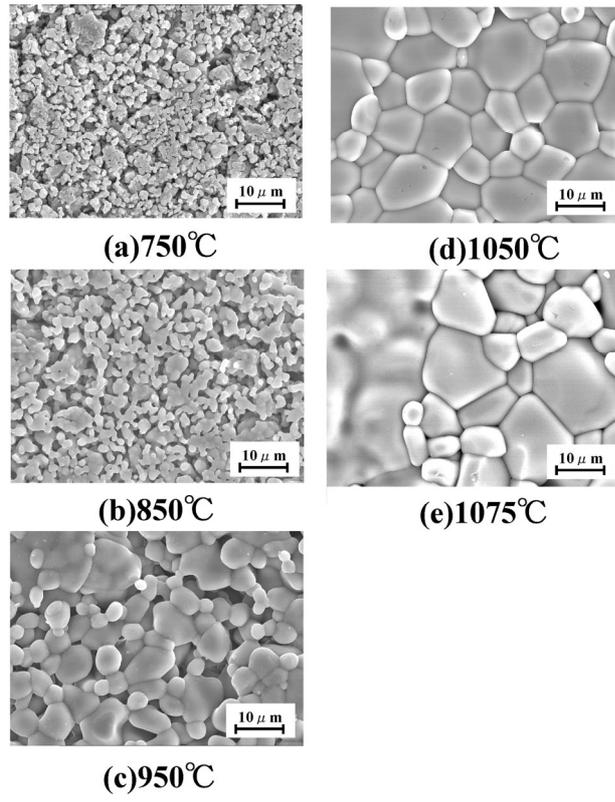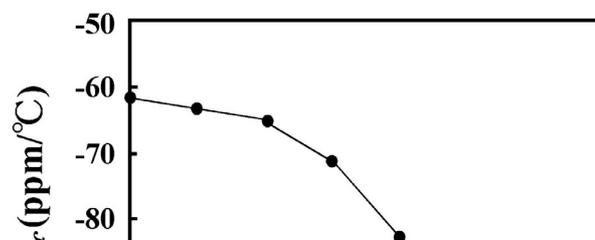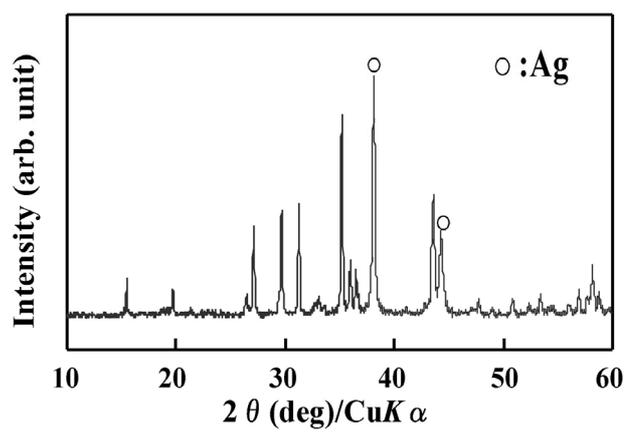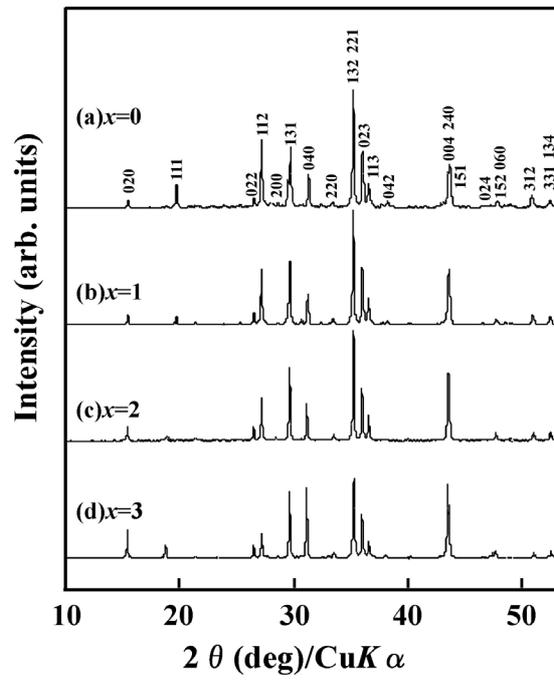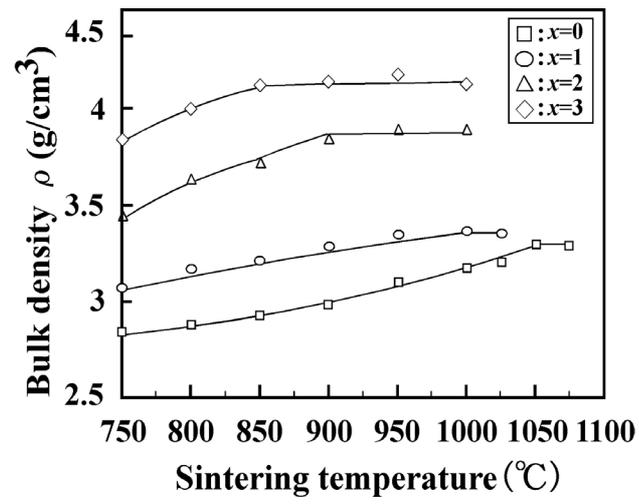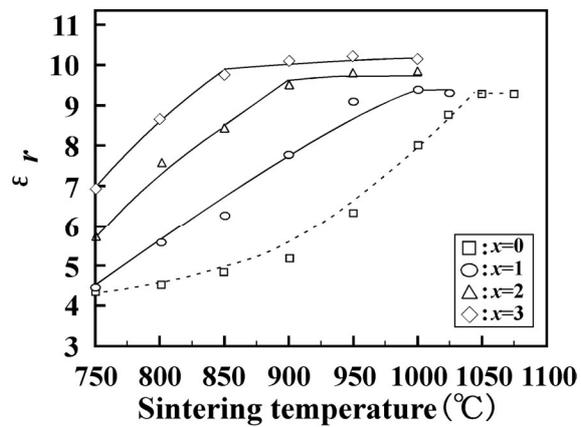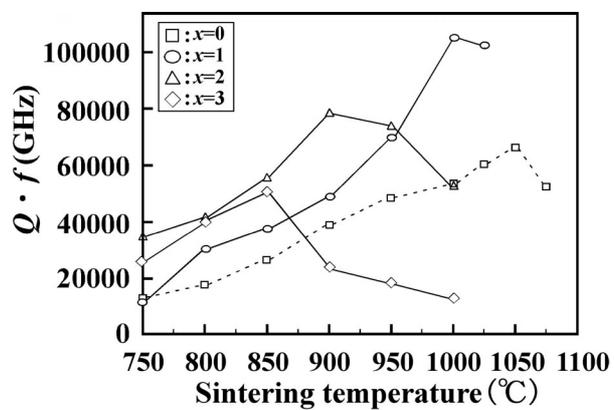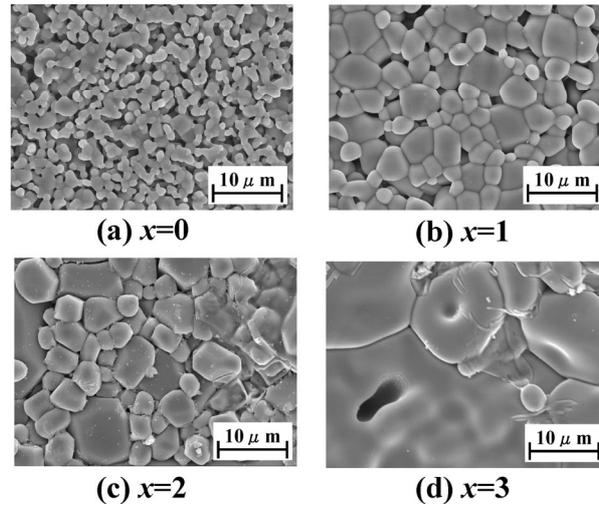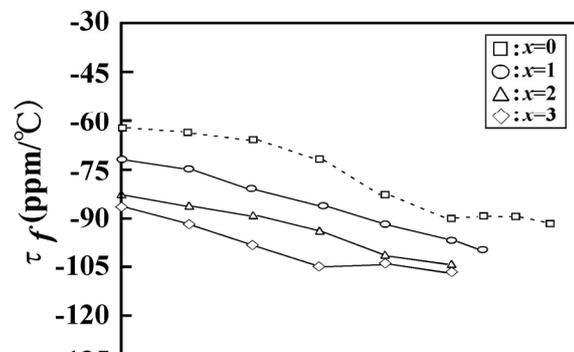
Fig.10

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

Sintering time (h)	ρ (g/cm^3)	ε_r	$Q \cdot f$ (GHz)	τ_f (ppm/℃)
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

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