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Microwave dielectric properties of $MgCo_2(VO_4)_2$ ceramics synthesized by a sol–gel method

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Abstract

$MgCo_2(VO_4)_2$ (MCV) ceramics have been prepared by a sol–gel method as potential candidates for use in microwave applications as a low-temperature co-fired ceramic (LTCC). The sintering and microwave dielectric properties of sol–gel processed MCV were compared with those of solid-state reaction processed MCV. The results showed that sol–gel processed MCV had a higher sinterability due to its much finer particle size. The sol–gel processed MCV was also found to have superior microwave dielectric properties compared with solid-state reaction processed MCV especially at low sintering temperatures.

Keywords: Powders-chemical preparation; X-ray methods; Dielectric properties; MgO

1. Introduction

The rapid progress in mobile and satellite communication system has created a high demand for the development of dielectric materials for microwave frequencies. Recently, multilayer structures have been extensively developed to miniaturize dielectric devices for high volume efficiency. In order to fabricate multilayer microwave devices, it is necessary to use low temperature co-fired ceramic (LTCC) because the dielectric ceramics and electrodes with low resistivity, such as Ag, should be co-sintered. Thus, dielectric ceramics should necessarily be sintered at temperatures below the melting point (961 °C) of Ag.

There are several approaches[1–5] to reduce the sintering temperature of dielectric ceramics: the addition of low melting point compounds such as B_2O_3, Bi_2O_3, and V_2O_5, the development of new compositions of LTCC materials, and chemical processing to produce smaller particle size of starting powders. There have been relatively few investigations[6] of chemical processing methods such as sol–gel and coprecipitation processes for producing LTCC for microwave applications. Most microwave dielectric materials are produced by a conventional solid-state reaction process.

A recent study[7] showed that $Mg_{3-x}Co_x(VO_4)_2$ ceramics, produced by a conventional solid-state reaction process, had a high $Q \times f_o$ value at a low sintering temperature (below 950 °C) with optimum microwave dielectric properties when $x = 2$. In order to study the effect of processing method on the microwave properties of LTCC, we produced $MgCo_2(VO_4)_2$ (MCV) ceramics by the sol–gel method and compared the results with those of MCV prepared by a conventional solid-state reaction method. The sol–gel method is undoubtedly a useful process for producing powders with a good control over stoichiometry and homogeneity, yielding very fine particle size as can be seen in the synthesis of $MgTi_2O_5$.[8] The sintering and microwave dielectric properties of the sol–gel processed MCV system at various sintering temperatures were studied.

2. Experimental method

Magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$, cobalt(II) nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$, and vanadium acetylacetonate $V(CH_3COCHCOCH_3)_3$ (Strem Chemicals) with 98% purity were used as the starting materials for sol–gel processing. The MCV precursor solution was prepared by dissolving stoichiometric quantities (1:2:2 molar ratio) of $Mg(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $V(CH_3COCHCOCH_3)_3$ in a mixed binary solvent of acetic acid and methyl alcohol (4:1 volume ratio). The final concentration was adjusted to produce 0.5 M solu-

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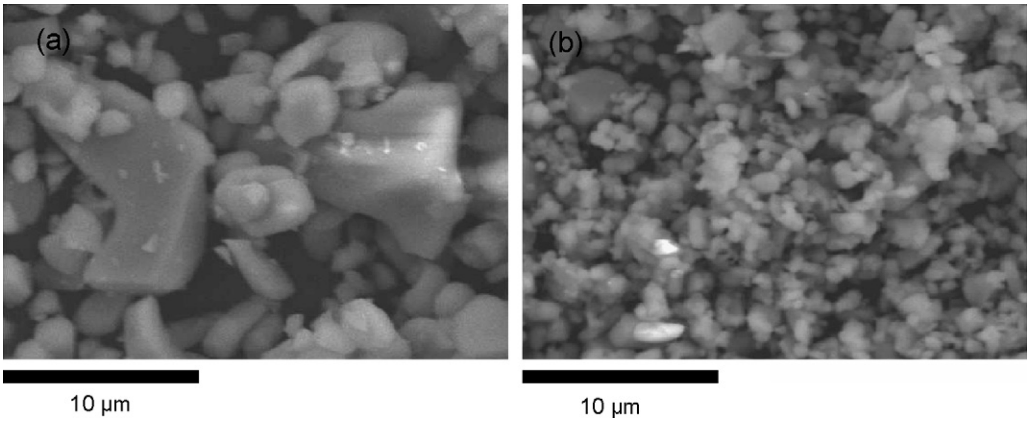

Fig. 1. SEM micrographs of MCV powders produced by (a) solid-state reaction process and (b) sol–gel process. Powders were calcined at 700 °C for 10 h.

tion and the solution was stirred with a magnetic stirrer for 1 h. After achieving complete dissolution, the resultant solution was heated at 90 °C to remove excess solvents. With continued heating at 90 °C for 1 h, the solution became highly viscous and finally MCV gels were formed. The dry gels were calcined at 700 °C for 10 h in air and milled for 24 h with zirconia balls. MCV powders were also prepared using a conventional solid-state reaction method. MgO, CoO, and V_2O_5 (High Purity Chemicals) with 99.9% purity were weighed and then mixed in deionized water for 24 h using conventional ball milling with zirconia balls. The mixed powders were subsequently calcined at 700 °C for 10 h in air and then milled for 24 h with zirconia balls. The ground powders from sol–gel and solid-state reaction process, respectively, were dried and pressed into pellets, 15 mm in diameter and 6.7 mm thick. The pellets were sintered at a temperature range of 750–930 °C for 5 h in air. The heating rate was 10 °C/min.

The morphology of the powders and the microstructure of the sintered MCV were examined using scanning electron microscopy (JSM 5310, JEOL) and phase identification of the sintered specimens was performed using X-ray diffractometry (D/MAX-2200, Rigaku). The shrinkage behavior was investigated by dilatometry (DIL420PC, Netzsch) at various temperatures up to 1050 °C with a heating rate of 10 °C/min in air. The densities were measured using the Archimedes method. The microwave dielectric properties were measured by the resonant cavity method described by Hakki and Coleman[9] using the TE_{011} propagation mode. The value of the temperature coefficient of resonant frequency (τ_f) was measured over a temperature range of −20 to 80 °C.

3. Results and discussion

SEM micrographs of MCV powders calcined at 700 °C for 10 h are given in Fig. 1. While the powders produced by conventional solid-state reaction process have many particles larger than 5 μm (Fig. 1(a)), the powders produced by sol–gel process obviously have much smaller particle size, <1 μm (Fig. 1(b)).

Dilatometer analysis for the MCV powders was conducted at a heating rate of 10 °C/min (Fig. 2). The onset temperature shifted to a lower temperature and maximum shrinkage moved to a higher value for the MCV produced by sol–gel processing. This increase in the sinterability is attributed to the smaller particle size of the sol–gel processed MCV.

The effect of the sintering temperature on the density and microwave dielectric properties of sol–gel processed MCV is shown in Fig. 3. The bulk densities of MCV increased from 3.51 to 4.12 g/cm^3 as the sintering temperature increased from 750 to 930 °C. The value of ε_r increased as the sintering temperature increased, with a maximum value of 10.34 at 930 °C. The increase of ε_r is attributed to the increase in the density. $Q \times f_o$ value increased as the sintering temperature increased and reached its maximum value of 55,740 GHz at 930 °C. The increase in the $Q \times f_o$ value is related to the increase in relative density and grain growth as reported in previous studies.[10,11] τ_f decreased from −10 to −85 ppm/°C as the sintering temperature increased from 750 to 930 °C. An improvement in τ_f would be needed for commercial application.

In Table 1, the density and microwave dielectric properties of MCV produced by two processes, solid-state reaction and

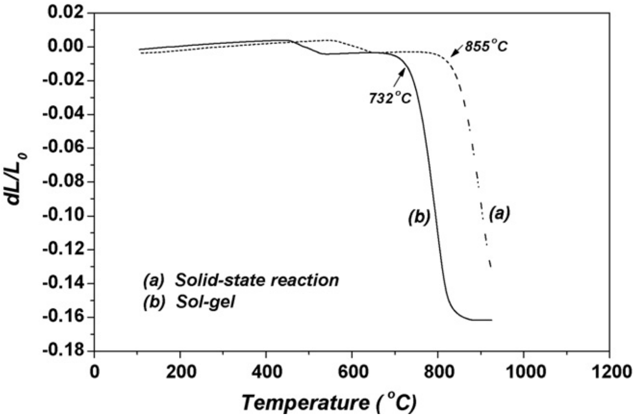

Fig. 2. Shrinkage profiles of MCV powders produced by (a) solid-state reaction process and (b) sol–gel process.

Table 1
Comparison of sintered densities and microwave dielectric properties of solid-state reaction and sol–gel processed MCV sintered in the temperature range 750–930 °C for 5 h

Sintering temperature/time	Bulk density (g/cm^3)		ε_r		$Q \times f_o$ (GHz)		τ_f (ppm/°C)	
	SS	SG	SS	SG	SS	SG	SS	SG
750 °C/5 h	×	3.51	×	9.12	×	34,500	×	−10
800 °C/5 h	3.0	3.90	7.1	10.10	19,500	45,600	−15	−16
850 °C/5 h	3.5	4.05	8.0	10.30	43,040	52,050	−46	−50
900 °C/5 h	3.7	4.10	9.3	10.31	48,020	55,340	−53	−55
930 °C/5 h	3.9	4.12	9.6	10.34	55,310	55,740	−83	−85

SS: solid-state reaction; SG: sol–gel; ×: not sintered.

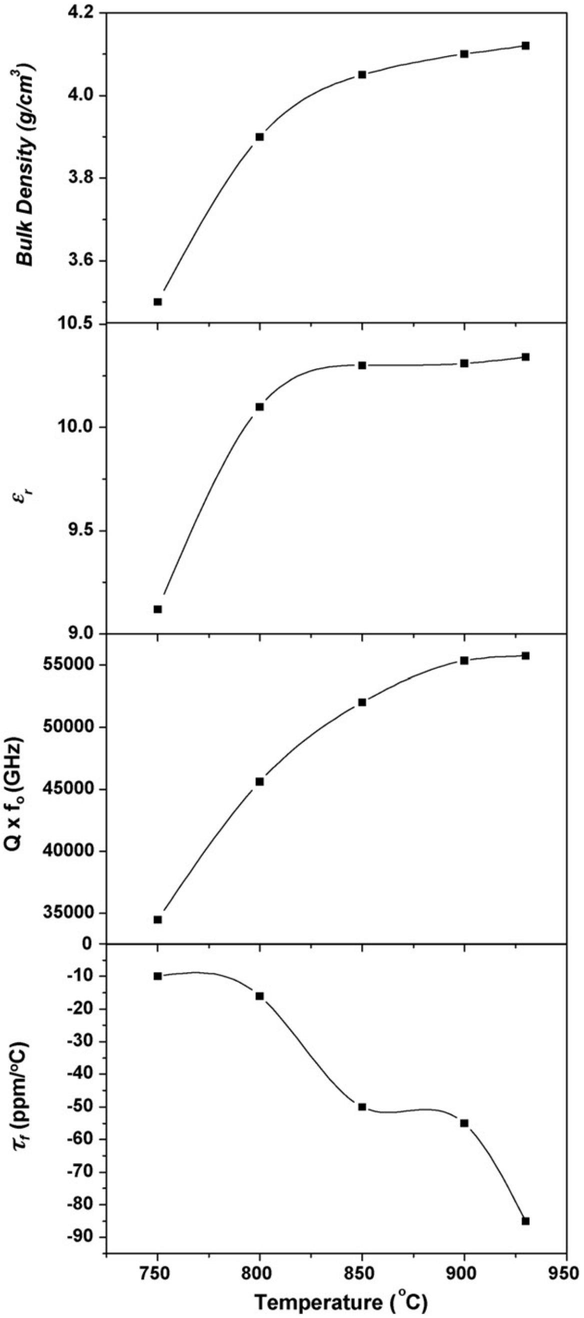

Fig. 3. Sintered densities and microwave dielectric properties of sol–gel processed MCV as a function of sintering temperature.

sol–gel, are compared. The bulk densities of sol–gel processed MCV were higher and the difference in density between the sol–gel and the solid-state reaction produced materials was bigger at lower sintering temperature. MCV produced by solid-state reaction did not densify at 750 °C. Since ε_r is related to the density, the same trend was observed for ε_r. While the $Q \times f_o$ values of MCV produced by the two routes were about the same at the highest sintering temperature, 930 °C, the difference increased as sintering temperature decreased. This difference is attributed to the poor densification and grain growth of solid-state reaction processed MCV. τ_f values were similar and the difference was not significant apart from at a sintering temperature of 750 °C where the solid-state reaction processed MCV did not densify at all. Umemura et al.[7] also studied MCV system ceramics produced by a conventional solid-state reaction process. While the $Q \times f_o$ values of the sol–gel produced MCV in this study are slightly lower, compared with their results at high sintering temperatures (>850 °C), all values are higher for the sol–gel processed MCV at lower sintering temperatures, 750 and 800 °C. The results are attributed to the higher sinterabilty of the sol–gel produced MCV due to the smaller particle size.

Fig. 4 shows the SEM microstructure of sol–gel processed MCV sintered at 750, 800, 850, and 930 °C for 5 h, respectively. The grain size measured by a linear intercept method increases from 0.8 to 9.5 μm with increasing sintering temperature. The apparent porosity of MCV decreased as the sintering temperature was increased. This observation is consistent with the results of the increase in $Q \times f_o$ value with increasing sintering temperatures.

Fig. 5 shows the XRD patterns of MCV, sintered at different temperatures (750, 800, 850, 900, and 930 °C) for 5 h. The MCV ceramics were found to be single phase without any secondary phase observed over the whole sintering temperature range within the limits of XRD analysis.

For the commercial application of LTCC, the reaction between the microwave dielectric materials and electrode should be minimized. XRD analysis of the dielectric ceramics and electrode powder mixture sintered at the desired temperature is considered an acceptable way to analyze the interface reaction.[12] This method is widely used for the investigation of any reaction between dielectrics and electrode materials used in multilayer chip capacitors. The XRD patterns of the sol–gel processed MCV powders, and the mixture of MCV

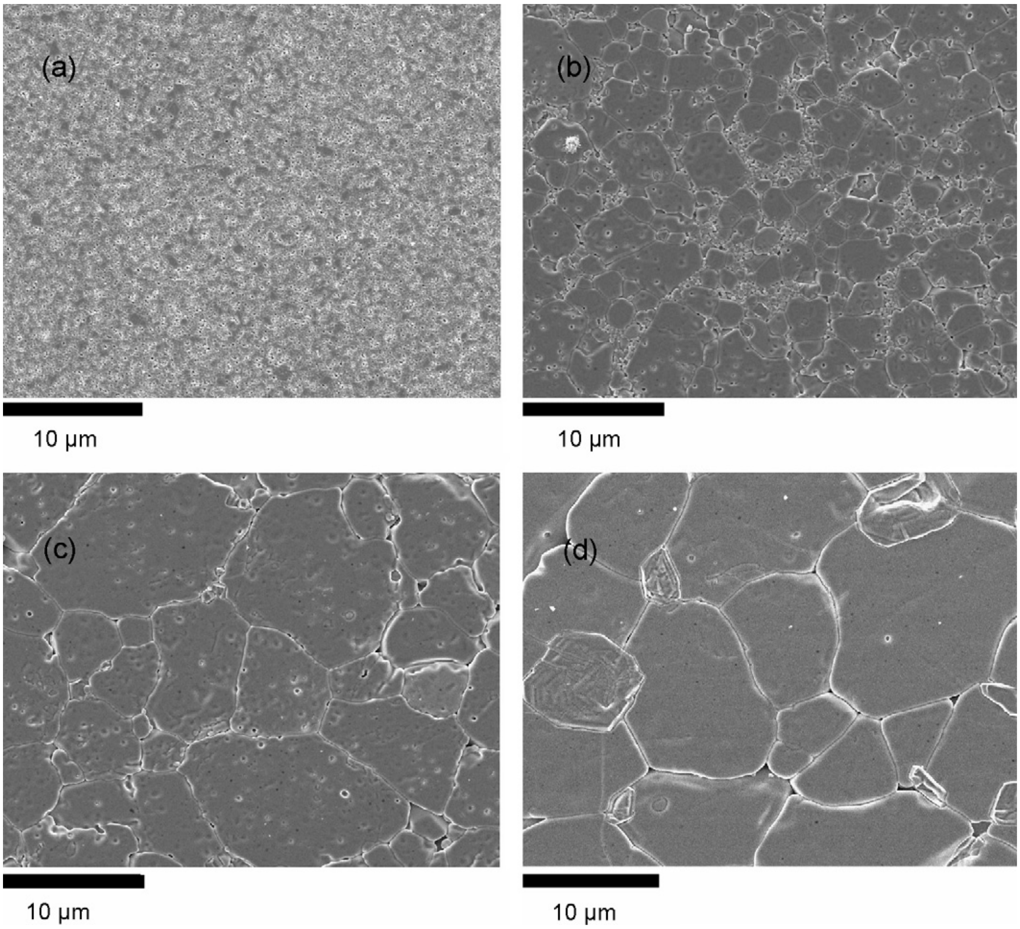

Fig. 4. SEM micrographs of sol–gel processed MCV sintered at (a) 750 °C, (b) 800 °C, (c) 850 °C, and (d) 930 °C for 5 h.

and Ag powders after the heat treatment at 900 °C for 5 h are shown in Fig. 6. Since the formation of a secondary phase was not observed in the XRD pattern, it is suggested that MCV has chemical compatibility with a Ag electrode, making Ag a showy candidate for use as an electrode for MCV system.

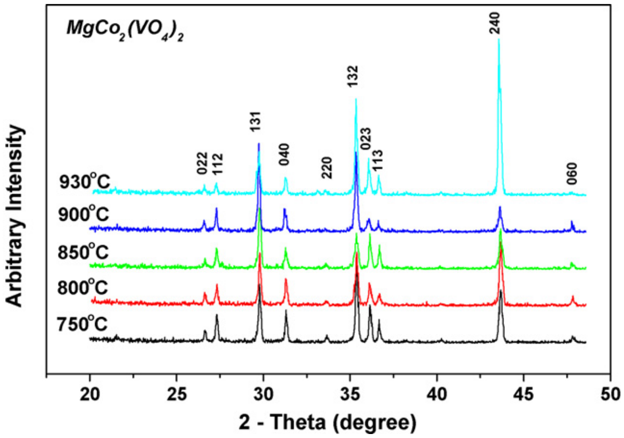

Fig. 5. XRD patterns of sol–gel processed MCV as a function of sintering temperature.

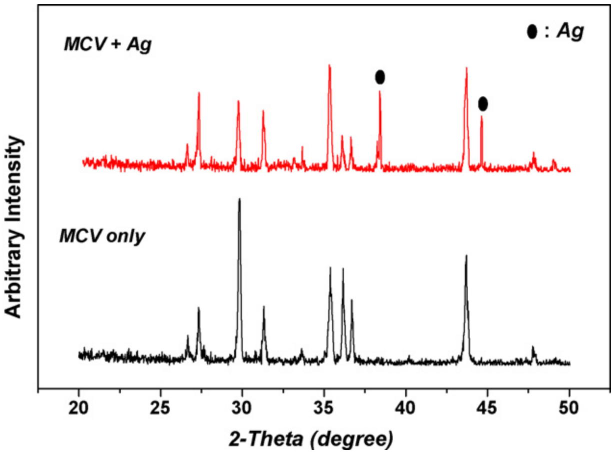

Fig. 6. XRD patterns of the sol–gel processed MCV powders, and the mixture of sol–gel processed MCV and Ag powders heat treated at 900 °C for 5 h.

4. Conclusions

The sintering performance and microwave dielectric properties of MCV prepared by a sol–gel method were investigated in order to identify the possibility of using it as a LTCC material for microwave applications. Due to the finer particle size (<1 μm) of the sol–gel processed MCV, it showed much higher sinterability than convention solid-state reaction processed MCV. A $Q \times f_o$ value of 55,740 GHz with a ε_r of 10.34 and a τ_f of −85 ppm/ °C were obtained for the sol–gel processed MCV after sintering at 930 °C for 5 h. The sol–gel processed MCV was shown to have a high $Q \times f_o$ value even at very low sintering temperature: 34,500 GHz at 750 °C for 5 h. MCV was found to chemically compatible with Ag electrode material; no secondary phase was observed in the XRD pattern of a mixture of MCV and Ag powder after heat-treated at 900 °C for 5 h. Thus, sol–gel processed MCV are considered to be an appropriate candidate as an LTCC material for microwave applications.

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References

1. Choi, Y., Park, J., Ko, W., Park, J., Mahm, S. and Park, J., Low temperature sintering of $BaTi_4O_9$-based middle-k dielectric composition for LTCC applications. *J. Electroceram.*, 2005, **14**, 157–162.
2. Kim, D., Kim, J., Yoon, S., Hong, K. and Kim, C., Microwave dielectric properties of low-fired $Ba_5Nb_4O_{15}$. *Am. Ceram. Soc.*, 2002, **85**, 2759–2762.
3. Huang, C., Weng, M., Lion, C. and Wu, C., Low temperature sintering and microwave dielectric properties of $Ba_2Ti_9O_{20}$ ceramics using glass additions. *Mater. Res. Bull.*, 2000, **35**, 2445–2456.
4. Kim, H., Kim, S., Nahm, S. and Byun, J., Low-temperature sintering and microwave dielectric properties of zinc metatitanate-rutile mixtures using boron. *Am. Ceram. Soc.*, 1999, **82**, 3043–3048.
5. Kim, H., Nahm, S., Byun, J. and Kim, Y., Low-fired (Zn Mg)TiO_3 microwave dielectrics. *Am. Ceram. Soc.*, 1999, **82**, 3476–3480.
6. Tang, X., Liu, J., Kwok, K. and Chan, H., Microwave dielectric properties of sol–gel derived $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$:B_2O_3 ceramics. *J. Electroceram.*, 2005, **14**, 119–122.
7. Umemura, R., Ogawa, H., Ohsato, H., Kan, A. and Yokoi, A., Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2O_2$ ceramic. *J. Eur. Ceram. Soc.*, 2005, **25**, 2865–2870.
8. Prasadarao, A., Selvaraj, U., Komarneni, S., Bhalla, A. and Roy, R., Enhanced densification by seeding sol–gel-derived aluminum titanate. *Am. Ceram. Soc.*, 1992, **75**, 1529–1533.
9. Hakki, B. and Coleman, P., A dielectric resonator method of measuring inductive in the millimeter range. *IRE Trans. Microwave Theory Tech. MTT*, 1960, **8**, 402–410.
10. Yang, J., Nahm, S., Choi, C., Lee, H. and Park, H., Microstructure and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with ZrO_2 addition. *Am. Ceram. Soc.*, 2002, **85**, 165–168.
11. Kucheiko, S., Choi, J., Kim, H. and Jung, H., Microwave dielectric properties of $CaTiO_3$-$Ca(Al_{1/2}Ta_{1/2})O_3$ ceramics. *Am. Ceram. Soc.*, 1996, **79**, 2739–2743.
12. Cho, S., Kim, C., Kim, D. and Hong, K., Dielectric properties of $Ln(Mg_{1/2}Ti_{1/2})O_3$ as substrates for high-T_c superconductor thin-films. *J. Mater. Res.*, 1999, **14**, 2484–2487.