Journal of Alloys and Compounds 509 (2011) 9650–9653

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Elucidating the dielectric properties of Mg_2SnO_4 ceramics at microwave frequency

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ARTICLE INFO

Article history:
Received 2 September 2010
Received in revised form 18 July 2011
Accepted 21 July 2011
Available online 28 July 2011

Keywords:
Mg_2SnO_4
Dielectric constant
Quality factor
Temperature coefficient of resonant frequency

ABSTRACT

This study investigated the potential applications of microwave dielectric properties of Mg_2SnO_4 ceramics in mobile communication. Mg_2SnO_4 ceramics were prepared using a conventional solid-state method. The X-ray diffraction patterns of the Mg_2SnO_4 ceramics revealed no significant variation of phase with sintering temperature. A maximum density of 4.62 g/cm^3, a dielectric constant (ε_r) of 8.41, a quality factor ($Q \times f$) of 55,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of −62 ppm/°C were obtained when Mg_2SnO_4 ceramics were sintered at 1550 °C for 4 h.

1. Introduction

The use of microwave ceramics in resonators, filters, and antennas in wireless communication systems such as wireless local area networks (WLAN) and global positioning systems (GPS), has been increasing rapidly in the last decade. Numerous investigations have focused on developing good microwave dielectric materials to miniaturize devices and stabilize system. Materials that are to be used 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 to be fabricated [1,2]. However, the carrier frequencies of interest are from the ISM (industrial, scientific and medical) bands to values that correspond to millimeter wavelengths. Materials with low dielectric constants are being introduced to replace materials with high dielectric constants in the millimeter wave range.

According to previous studies, MO-SnO_2 (M = Ca, Sr, and Ba) ceramics are associated with their low dielectric constant and small loss tangent [3–5]. $CaSnO_3$ and $SrSnO_3$ ceramics also have a low temperature coefficient of the dielectric constant in the frequency range from 5 Hz to 13 MHz. These materials are highly promising strong potential for application in a low-capacitance components that must be stable at high temperature [3,4]. Mg_2SnO_4 ceramics exhibit a dielectric constant of 8, a loss factor of 9.31×10^{-3}, and a temperature coefficient of dielectric constant of −53.9 ppm/°C at 1 MHz when sintered at 1600 °C for 4 h [5]. However, no technical information on the microwave dielectric properties of Mg_2SnO_4 ceramics is available in the published literature. This fact motivates this investigation of the microwave dielectric properties of Mg_2SnO_4 ceramics.

Mg_2SnO_4 ceramics were synthesized herein using the conventional mixed-oxide method. The effect of the sintering temperature on the microwave dielectric properties of Mg_2SnO_4 ceramics was explored. The dielectric properties of the Mg_2SnO_4 ceramics at microwave frequencies were found to vary with the sintering temperatures. To elucidate further these different microwave dielectric properties, they were analyzed by densification and X-ray diffraction (XRD), and microstructural observations were made.

2. Experimental procedure

The starting raw chemicals were MgO (99.3%) and SnO_2 (99.0%) powders. The prepared compound was Mg_2SnO_4. 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 1200 °C for 4 h. The calcined powder was re-milled for 12 h using PVA solution as a binder. The obtained powder was then crushed into a fine powder through a sieve with a 200 mesh. It 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 1450–1600 °C for 4 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. X-ray Rigaku D/MAX-2200 spectrometer was used with Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of

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doi:10.1016/j.jallcom.2011.07.065

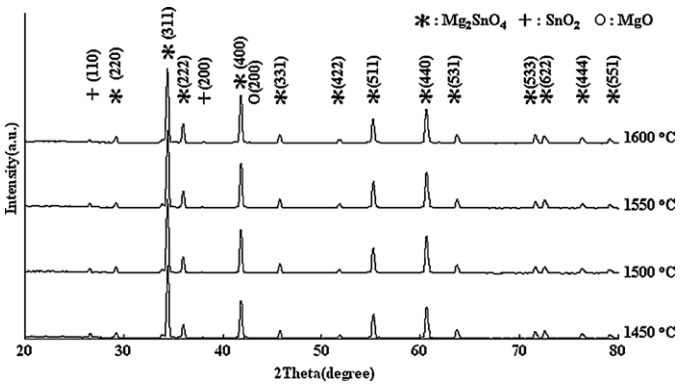

Fig. 1. X-ray diffraction patterns of Mg_2SnO_4 ceramics sintered at 1450–1600 °C for 4 h.

20–80°. Scanning electron microscopy (SEM; JEOL JSM-6500F) and energy dispersive X-ray spectrometer (EDS) were carried out to examine the microstructures of the specimens. The apparent densities of the specimens were measured using the liquid Archimedes method using distilled water.

The microwave dielectric properties of the specimens were measured using the postresonator method that was developed by Hakki and Coleman [6]. The postresonator scheme utilizes a specimen in the form of a cylinder of diameter D and length L. The specimens whose microwave dielectric property was measured had an aspect ratio D/L of approximately 1.6, which is in the range indentified as acceptable by Kobayashi and Katoh [7]. The cylindrical resonator was sandwiched between two conducting plates. Two small antennas were positioned in the vicinity of the specimen to couple the microwave signal power into or out of the resonator. The other ends of the antennas were connected to an Agilent E5071C network analyzer. The resonance characteristics depended on the size and dielectric properties of the specimen. The microwave energy was coupled using electric-field probes. The TE_{011} resonant mode was optimal for determining the dielectric constant and the loss factor of the specimen. The Agilent E5071C network analyzer was used to identify the TE_{011} resonant frequency of the dielectric resonator, and the dielectric constant and quality factor were calculated. 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) was 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.

3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of Mg_2SnO_4 ceramics that were sintered at 1450–1600 °C for 4 h. Clearly, Mg_2SnO_4 is the main crystalline phase, which is accompanied by small amounts of MgO and SnO_2 as secondary phases, indicating that some of the $MgSnO_3$ might have formed in the initial stages. The parallel reactions are as follows:

$$MgO + SnO_2 \rightarrow MgSnO_3 \quad (2)$$

and

$$2MgO + SnO_2 \rightarrow Mg_2SnO_4 \quad (3)$$

$MgSnO_3$ is unstable at high temperatures and thermally decomposes into Mg_2SnO_4 and SnO_2.

$$MgSnO_3 \rightarrow 0.5Mg_2SnO_4 + 0.5SnO_2 \quad (4)$$

These results are consistent with those of Pfaff [8]. The SnO_2 intensity declined at high sintering temperature, revealing evaporation of SnO_2 at high temperatures according to the reaction [9]:

$$SnO_2(s) \rightarrow SnO(g) + 0.5O_2(g) \quad (5)$$

The relative integrated intensities demonstrated the difference in amounts of Mg_2SnO_4, SnO_2, and MgO more clearly [10]. The relative integrated densities can be assumed to be represented the amount of phases presented. The relative integrated intensities of Mg_2SnO_4, SnO_2, and MgO were evaluated from most intensive lines of each phase. For example, the relative integrated intensity of Mg_2SnO_4 was calculated as follows:

$$\text{Relative intensity of } Mg_2SnO_4 = \frac{I_{Mg_2SnO_4(3\ 1\ 1)}}{I_{Mg_2SnO_4(3\ 1\ 1)} + I_{SnO_2(1\ 1\ 0)} + I_{MgO(2\ 0\ 0)}} \times 100 \quad (6)$$

Table 1
Amount of Mg_2SnO_4, SnO_2, and MgO sintered at 1450–1600 °C for 4 h.

Sintering temperature (°C)	Mg_2SnO_4 (%)	SnO_2 (%)	MgO (%)
1450	92.13	6.49	1.38
1500	91.74	6.74	1.52
1550	92.12	6.37	1.51
1600	93.34	4.71	1.95

Table 1 shows the amount of SnO_2 decreased significantly from 6.37% to 4.71% as the sintering temperature increased from 1550 to 1600 °C, which is in agreement with Eq. (5). The variation of the amounts of Mg_2SnO_4 and MgO with sintering temperature was not significant compared with that of SnO_2. The formation of second phases of SnO_2 and MgO affected the microwave dielectric properties of Mg_2SnO_4 ceramics.

Fig. 2 shows the microstructures of Mg_2SnO_4 ceramics that were sintered at various temperatures for 4 h. As the sintering temperature was increased from 1450 to 1550 °C, the pores of the Mg_2SnO_4 ceramics almost disappeared upon sintering at 1550 °C. Non-uniform grain growth occurred at high sintering temperature (1600 °C), potentially degrading the microwave dielectric properties of the Mg_2SnO_4 ceramics. The pores and non-uniform grain growth may have influenced the microwave dielectric properties of the Mg_2SnO_4 ceramics. To identify the compositions of the second phases, an energy-disperse spectroscopy (EDS) analysis of the grains of Mg_2SnO_4 ceramics that were sintered at 1500 °C for 4 h was carried out, as shown in Fig. 2. According to the quantitative analysis, as shown in Table 2, the A and B grains are Mg_2SnO_4, the C and D grains are MgO, and the E grain is SnO_2.

Fig. 3 displays the apparent densities and dielectric constants of the Mg_2SnO_4 ceramics that were sintered at 1450–1600 °C for 4 h. The apparent density of the Mg_2SnO_4 ceramics that were sintered at 1450–1600 °C for 4 h was highest, 4.62 g/cm^3, when sintering was conducted at 1550 °C, beyond which temperature, it declined. The increase in apparent density may be caused by the decrease in the number of pores, and the decline in apparent density may be caused by the non-uniform grain growth, as presented in Fig. 2. The relationship between the dielectric constant and the sintering temperature was similar to that between the apparent density and the sintering temperature. The dielectric constant of Mg_2SnO_4 ceramics increased from 8.28 to 8.41 as the temperature of sintering increased from 1450 to 1550 °C. However, it fell from 8.41 to 8.27 as the sintering temperature increased from 1550 to 1600 °C for 4 h. The Mg_2SnO_4 ceramics that were sintered at 1550 °C for 4 h had the highest dielectric constant of 8.41. The increase in dielectric constant was associated with the increase in the density of the ceramics. A higher density is associated with a lower porosity and,

Table 2
EDS data of grains of Mg_2SnO_4 ceramics sintered at 1500 °C for 4 h.

Atomic element	Mg (%)	Sn (%)	O (%)
A	20.94	10.88	68.18
B	20.89	9.82	69.29
C	40.8	0	59.2
D	35.08	0	64.92
E	0	44.04	55.96

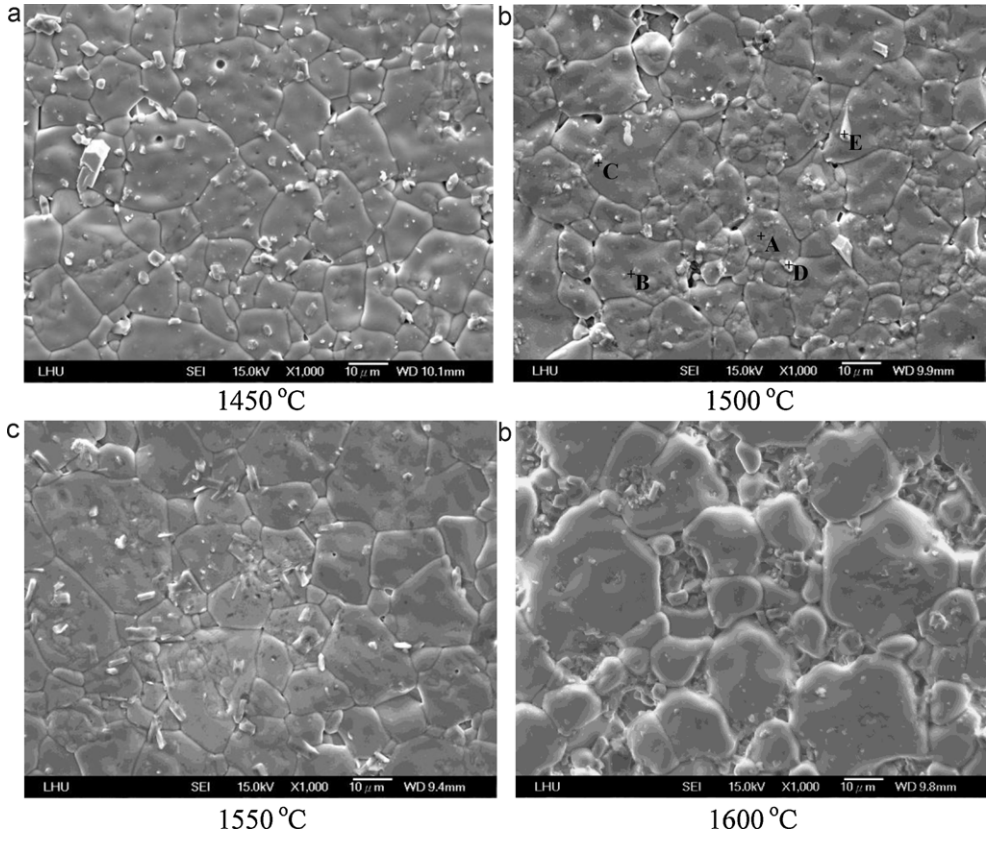

Fig. 2. Microstructures of Mg_2SnO_4 ceramics sintered at different temperatures for 4 h: (a) 1450 °C, (b) 1500 °C, (c) 1550 °C and (d) 1600 °C.

therefore, a higher dielectric constant. However, the apparent density of the specimens sintered at 1600 °C for 4 h was higher than those at 1450 and 1500 °C. The dielectric constant of the specimens sintered at 1600 °C was lower than those at 1450 and 1500 °C. This fact may be explained by the second phases. The second phases are extrinsic factor in controlling the dielectric constant. The dielectric constant of the composites can be calculated by the mixture rule:

$$\mathrm{Ln}\,\varepsilon_r(x) = v_1\,\mathrm{Ln}\,\varepsilon_{r1} + v_2\,\mathrm{Ln}\,\varepsilon_{r2} + v_3\,\mathrm{Ln}\,\varepsilon_{r3} \quad (7)$$

where ε_r is the dielectric constant of the composite, V_1, V_2, and V_3 are the volume fractions of Mg_2SnO_4, SnO_2, and MgO, respectively, and ε_{r1}, ε_{r2} and ε_{r3} are the dielectric constants of Mg_2SnO_4, SnO_2, and MgO, respectively. The dielectric constants of SnO_2 and MgO ceramics were 2630 and 7.92, respectively [11,12]. Since the amount of SnO_2 decreased from 6.37% to 4.71% and the amount of MgO increased from 1.51% to 1.95% as the sintering temperature increased from 1550 to 1600 °C as shown in Table 1, the dielectric constants of specimens is inferred to be decreased as sintering temperature increased from 1550 to 1600 °C.

Fig. 4 presents the $Q \times f$ and temperature coefficient of resonant frequency (τ_r) of the Mg_2SnO_4 ceramics that were sintered at 1450–1600 °C for 4 h. The $Q \times f$ of the Mg_2SnO_4 ceramics increased from 47,800 to 55,100 GHz as the temperature of sintering for 4 h increased from 1450 to 1550 °C. However, it decreased from 55,100

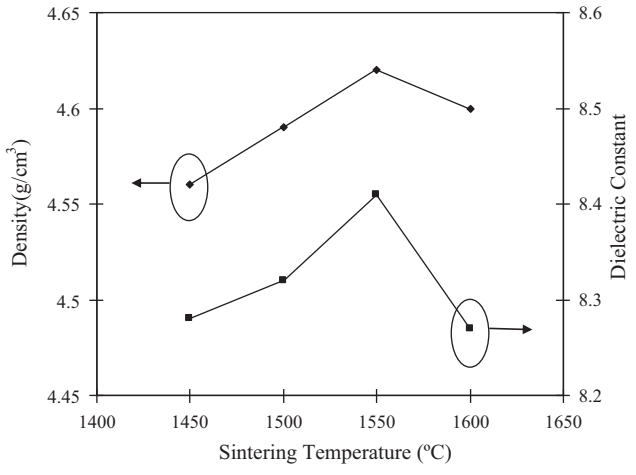

Fig. 3. Apparent densities and dielectric constant of Mg_2SnO_4 ceramics sintered at 1450–1600 °C for 4 h.

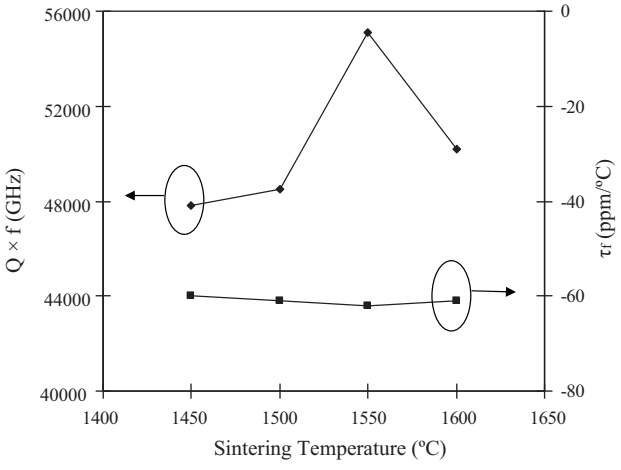

Fig. 4. $Q \times f$ and temperature coefficient of resonant frequency (τ_f) of Mg_2SnO_4 ceramics sintered at 1450–1600 °C for 4 h.

to 50,200 GHz as the temperature of sintering for 4 h increased from 1550 to 1600 °C. The highest $Q \times f$ of 55,100 GHz was obtained for Mg_2SnO_4 ceramics that were sintered at 1550 °C for 4 h. The relationship between the $Q \times f$ and the sintering temperature was consistent with that between the apparent density and the sintering temperature, because the microwave dielectric loss was affected by several factors, and consisted of intrinsic and extrinsic components. Intrinsic loss is associated with the lattice vibrational modes. Extrinsic loss is related to the density, porosity, second phases, impurities, oxygen vacancies, grain size and lattice defects [13,14]. Since the $Q \times f$ of Mg_2SnO_4 ceramics was consistent with the variation of the apparent density, it is suggested to be dominated by the apparent density. Generally, τ_f is related to the composition, the amount of additive, and the second phases that are present in ceramics [9]. A τ_f of −50 ppm/°C was obtained for MgO ceramics that were sintered at 1490 °C for 4 h [12]. The τ_f of MgO ceramics is less negative compared with that of Mg_2SnO_4 ceramics, implying the presence of the second phase shifted the τ_f of the specimen to the positive direction. Since the τ_f of the specimens sintered at 1600 °C was less negative compared with that at 1550 °C, the τ_f of SnO_2 is inferred to be negative compared with that of MgO. The τ_f of the specimens shifted to positive as the sintering temperature decreased from 1550 to 1450 °C for 4 h. This is associated with the fact that the temperature coefficient of the resonant frequency can be expressed by the sum of temperature coefficient of the dielectric constant and the coefficient of thermal expansion. The τ_f can be calculated by:

$$\tau_f = -\alpha_1 - \frac{1}{2}\tau_\varepsilon \tag{8}$$

where α_1 is the coefficient of thermal expansion and τ_ε is the temperature coefficient of dielectric constant. The temperature coefficient of dielectric constant (τ_ε) can be calculated by [15]:

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_P = \frac{(\varepsilon - 1)(\varepsilon + 2)}{\varepsilon}(A + B + C)$$
$$= \left(\varepsilon - \frac{2}{\varepsilon} + 1\right)(A + B + C) \tag{9}$$

$$A = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P, \quad B = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P,$$
$$C = \frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial T}\right)_V$$

The temperature coefficient of dielectric constant (τ_ε) depended on dielectric constant. The dielectric constant of Mg_2SnO_4 ceramics decreased as the sintering temperature decreased from 1550 to 1450 °C and, therefore, the absolute value of τ_f and τ_ε decreased as the sintering temperature decreased from 1550 to 1450 °C. A τ_f of −62 ppm/°C was measured for Mg_2SnO_4 ceramic that was sintered at 1550 °C for 4 h.

4. Conclusions

The microwave dielectric properties of Mg_2SnO_4 ceramics were examined. The X-ray diffraction patterns of the Mg_2SnO_4 ceramics did not significantly vary with sintering temperature. Mg_2SnO_4 ceramics that were sintered at 1550 °C for 4 h had an apparent density of 4.62 g/cm^3, a dielectric constant of 8.41, a $Q \times f$ of 55,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of −62 ppm/°C. Mg_2SnO_4 ceramics with a low dielectric constant had potential for application in the millimeter wave range.

Acknowledgment

The authors would like to thank the National Science Council in Taiwan for financially supporting this research under Contract no. NSC 100-2622-E-262-001-CC3.

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