Journal of Alloys and Compounds 509 (2011) 5829–5832

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Microwave dielectric properties and its compatibility with silver electrode of $Li_2MgTi_3O_8$ ceramics

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ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form 22 February 2011
Accepted 23 February 2011
Available online 3 March 2011

Keywords:
Electroceramics
$Li_2MgTi_3O_8$ ceramic
LTCC
Microwave dielectric properties

ABSTRACT

The effects of $BaCu(B_2O_5)$ (BCB) additions on the sintering temperature and microwave dielectric properties of $Li_2MgTi_3O_8$ ceramic have been investigated. The pure $Li_2MgTi_3O_8$ ceramic shows a relative high sintering temperature (~1000 °C) and good microwave dielectric properties as $Q \times f$ of 40,000 GHz, ε_r of 27.2, τ_f of 2.6 ppm/°C. It was found that the addition of a small amount of BCB can effectively lower the sintering temperature of $Li_2MgTi_3O_8$ ceramics from 1025 to 900 °C and induce no obvious degradation of the microwave dielectric properties. Typically, the 0.5 wt% BCB added $Li_2MgTi_3O_8$ ceramic sintered at 900 °C for 2 h exhibited good microwave dielectric properties of $Q \times f$ = 36,200 GHz (f = 7.31 GHz), ε_r = 26 and τ_f = −2 ppm/°C. Compatibility with Ag electrode indicates this material can be applied to low temperature-cofired ceramics (LTCC) devices.

1. Introduction

Development of communication systems such as mobile systems requires the miniaturization of device size. Recently, low temperature co-fired ceramic (LTCC) multilayer devices have been investigated to reduce the device size [1,2]. As a metallic electrode, Ag has been widely used in LTCC technology because of its high conductivity and comparatively low cost. The melting temperature of Ag is low, about 961 °C. Therefore, for the fabrication of the multilayer devices, it is important to develop microwave dielectric ceramics, which have a low sintering temperature and can be co-fired with Ag.

Most of the known commercial dielectric materials for the high-frequency applications have a good microwave dielectric properties, but they cannot be cofired with Ag electrode because of high sintering temperatures between 1200 °C and 1500 °C [3–7]. So, how to reduce their sintering temperatures to lower than the melting point of the Ag or Cu electrodes has aroused world-wide interest. Generally, three common methods have been used to reduce the sintering temperature of the dielectric ceramics: low-melting glass addition, chemical processing, and smaller particle sizes of starting materials. Among these methods, low-melting glass additions for liquid-phase sintering is lower in cost and easier to process than the other two. Low-temperature sintering of dielectric materials with glass addition has been successfully achieved by the several microwave dielectric ceramics systems such as $MgO–TiO_2$, $Li_2O–Nb_2O_5–TiO_2$, $CaO–Li_2O–Nb_2O_5–TiO_2$, etc. [8–15].

Within the $Li_2O–MgO–TiO_2$ system, the crystal structure of $Li_2MgTi_3O_8$ has been reported by Virginia [16]. More recently, George and Sebastian [17] first reported that this ceramic has good microwave dielectric properties of ε_r = 27.2, $Q \times f$ = 42,000 GHz and τ_f = 3.2 ppm/°C. Then they reported the same family of materials $Li_2Mg_{1-x}Zn_xTi_3O_8$ and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn), these materials also have good microwave dielectric properties [18]. Although the $Li_2MgTi_3O_8$ ceramic could be sintered to essentially full density at 1075 °C without sintering aids, further investigations are still required for lowering its sintering temperature to about 900 °C so that they could be co-fired with Ag electrode. George and Sebastian [19] reported that the lithium magnesium zinc borosilicate (LMZBS) glass-doped $Li_2MgTi_3O_8$ ceramic could be sintered at 925 °C, and showed the microwave dielectric properties of ε_r = 24.5, $Q \times f$ value = 44,000 GHz, τ_f = 0.2 ppm/°C.

It is well known that $BaCu(B_2O_5)$ addition often makes it possible to decrease the sintering temperature of many materials [20–23]. For example, using 6 mol.% BCB, the $Ba(Zn_{1/3}Nb_{2/3})O_3$ dielectric can be sintered at 875 °C and obtained good microwave dielectric properties with values of ε_r = 35, $Q \times f$ = 16,000 GHz and τ_f = 22.1 ppm/°C [23]. In this work, $BaCu(B_2O_5)$ additive was made and added to $Li_2MgTi_3O_8$ ceramics in order to investigate the possibility of using BCB as a low temperature sintering additive. Furthermore, its effect on the sintering temperature, microstructure and microwave dielectric properties of the $Li_2MgTi_3O_8$ ceramics was also investigated.

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doi:10.1016/j.jallcom.2011.02.134

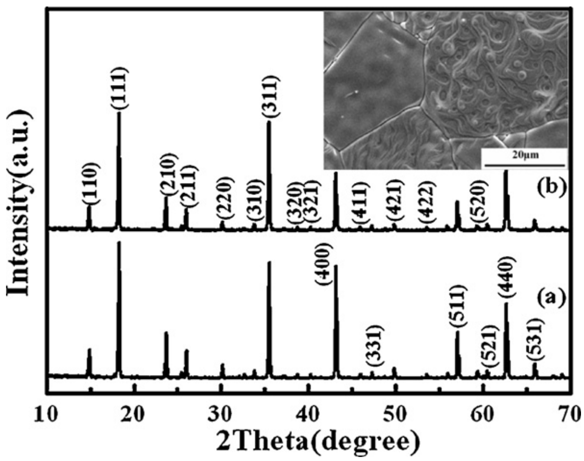

Fig. 1. X-ray diffraction patterns (XRD) of (a) powder calcined at 850 °C and (b) samples sintered at 1025 °C, Inset shows SEM photograph of $Li_2MgTi_3O_8$ samples sintered at 1025 °C for 2 h.

2. Experimental procedure

Specimens of the $Li_2MgTi_3O_8$ ceramics were prepared by a conventional mixed oxide route from the high-purity oxide powders (≥99.9%, Guo-Yao Co. Ltd., Shanghai, China) of Li_2CO_3, MgO and TiO_2. Stoichiometric proportions of the above raw materials were mixed in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 850 °C for 4 h. To synthesize the BCB ceramic powder, $Ba(OH)_2{\cdot}8H_2O$ (>99%, Guo-Yao Co. Ltd., Shanghai, China), CuO (>99%, Guo-Yao Co. Ltd., Shanghai, China) and H_3BO_3 (>99%, Guo-Yao Co. Ltd., Shanghai, China) were mixed for 4 h in a nylon jar with zirconia balls, then dried and calcined at 800 °C for 4 h. After subsequent ball-milling of LMT with 0–3.0 wt% BCB, the powders were uniaxially pressed into disks of 10 mm in diameter and 5 mm in thickness under the pressure of about 150 MPa. The pure $Li_2MgTi_3O_8$ pellets were sintered at 975–1150 °C for 2 h in air and the ceramic pellets added with BCB were sintered at 850–950 °C for 2 h in air.

The crystal structures of the specimens were analyzed by an X-ray diffractometer (Rigaku D/MAX-2400, Japan) with Cu K_α radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructural observation of the samples was performed using scanning electron microscopy (JEOL JSM-6460LV, Japan).

Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \tag{1}$$

where f_T, f_0 were the resonant frequencies at the measuring temperature T and T_0 (25 °C) respectively.

3. Results and discussion

The room-temperature XRD patterns recorded for the calcined powders at 850 °C and the ceramic sintered at 1025 °C for 2 h are shown in Fig. 1. A single-phase $Li_2MgTi_3O_8$ cubic structure (PDF File No. 01-089-1308) was formed and no secondary phase could be observed in the diffraction patterns. Its pattern could be indexed with a $P4_332(212)$ cubic cell with $a = 8.38057 \pm 0.00041$ Å, $V = 588.6$ Å^3, and $Z = 4$ (Z denotes the number of unit cell molecules in a unit cell), which agrees well with that reported by Virginia [16]. The theoretical density of the $Li_2MgTi_3O_8$ ceramic calculated from XRD data is about 3.50 g/cm^3. The SEM micrograph of the surface of $Li_2MgTi_3O_8$ ceramic sintered at 1025 °C is also shown in Fig. 1. The dense microstructure of $Li_2MgTi_3O_8$ ceramic sintered at 1025 °C for 2 h with only few pores existing can be confirmed by the SEM result.

Fig. 2 presents the apparent densities and relative densities of $Li_2MgTi_3O_8$ ceramics as a function of sintering temperature. As the sintering temperature increases from 975 to 1025 °C, the apparent density increases from 3.34 to 3.4 g/cm^3, which is equivalent to a relative density of about 97.2% of the theoretical density. When the sintering temperature further increases, the density of $Li_2MgTi_3O_8$ ceramics reaches saturation. This result indicates that the densification temperature of the $Li_2MgTi_3O_8$ ceramic is around 1025 °C.

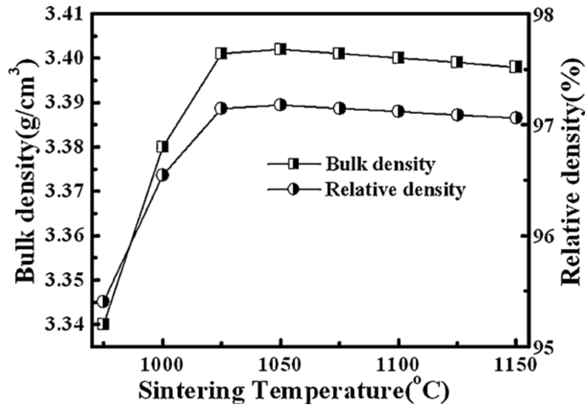

Fig. 2. Apparent densities and relative densities of $Li_2MgTi_3O_8$ ceramics as a function of sintering temperature.

The microwave dielectric properties of $Li_2MgTi_3O_8$ ceramics are shown in Fig. 3. The relative permittivity versus sintering temperature of $Li_2MgTi_3O_8$ ceramics has a trend similar to that of the apparent density. When the sintering temperature increases to 1025 °C, the relative permittivity reaches to a saturated value of about 27.2. The $Q \times f$ value of $Li_2MgTi_3O_8$ ceramics reaches the maximum with a value of about 40,000 GHz (at f = 6.2 GHz). The τ_f values do not change remarkably with increasing sintering temperature and remain stable at about 2.6 ppm/°C. In general, the $Li_2MgTi_3O_8$ ceramics sintered at 1025 °C have better microwave dielectric properties of $\varepsilon_r = 27.2$, $Q \times f = 40{,}000$ GHz, $\tau_f = 2.6$ ppm/°C.

Comparing with other glasses added to reduce the sintering temperature of the materials, $BaCu(B_2O_5)$ not only has a low sintering temperature (~810 °C) and low melting point (~850 °C), but also exhibits excellent microwave dielectric properties with permittivity of 7.4 $Q \times f$ values of 50,000 GHz and τ_f values of −32 ppm/°C [23]. To further reduce the sintering temperature of this new microwave dielectric ceramic, a small amount of $BaCu(B_2O_5)$ (BCB) has been added into the samples. Due to the liquid phase effect, the addition of BCB can efficiently lower the sintering temperature from 1025 to 900 °C. The XRD patterns of the BCB-added ceramics sintered at 900 °C are very similar to that of the pure ceramic and no secondary phase could be detected (as shown in Fig. 4). Fig. 5 illustrates the SEM micrographs of the $Li_2MgTi_3O_8$ ceramics added with different amounts of BCB sintered at 900 °C for 2 h. For the BCB added samples, dense microstructures were

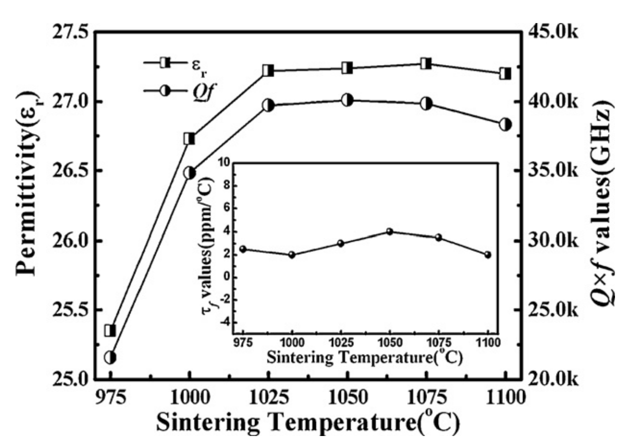

Fig. 3. The relative permittivity, $Q \times f$ values, and temperature coefficient of resonant frequency values of $Li_2MgTi_3O_8$ ceramics as a function of sintering temperature.

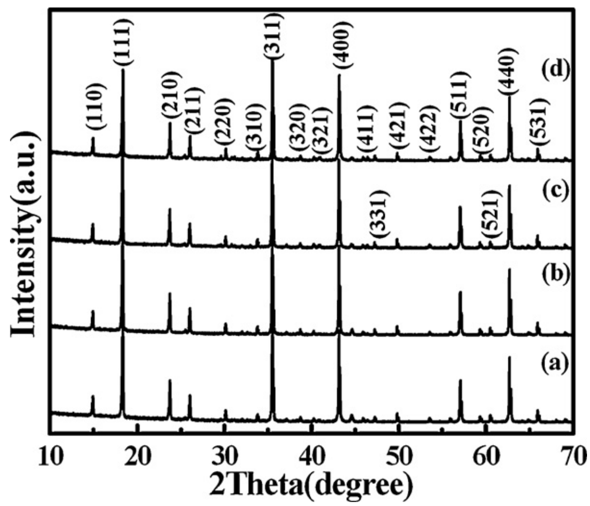

Fig. 4. X-ray diffraction patterns (XRD) of $Li_2MgTi_3O_8$ powders sintered at 900 °C for 2 h with: (a) 0.5 wt%, (b) 1.0 wt%, (c) 2.0 wt% and (d) 3.0 wt% BCB addition.

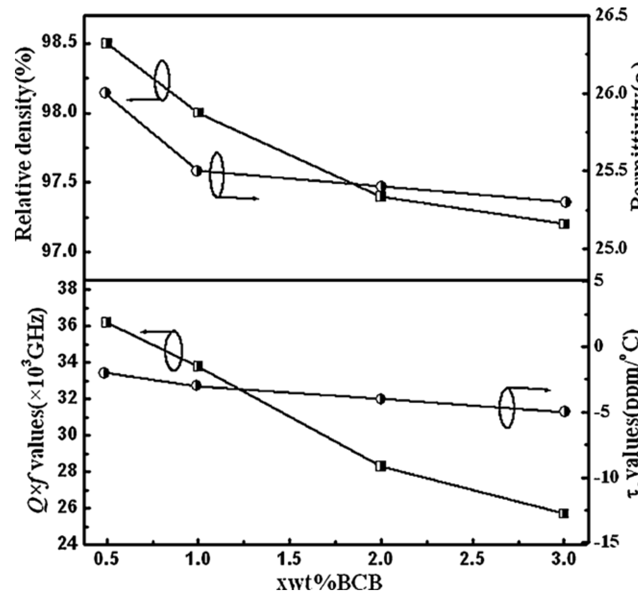

Fig. 6. Relative density, permittivity, $Q \times f$ values and τ_f values of BCB added $Li_2MgTi_3O_8$ powders sintered at 900 °C for 2 h.

formed. A reduced grain growth rate was observed since the sintering aid promoted the densification of ceramics while inhibited the grain growth due to a higher surface energy, so the grain sizes of the BCB-added samples are smaller than those of pure $Li_2MgTi_3O_8$ ceramic. Besides, the smaller grain sizes can also be due to the fact that the sintering temperature is decreased by about 125 °C.

Fig. 6 shows the relative densities and microwave dielectric properties of the pellets with the addition of 0.5–3 wt% BCB sintered at 900 °C. From Fig. 6, it can be seen that the densities of all the BCB added samples were higher than that of pure ceramic (3.4 g/cm^3), which means that the BCB is a very effective low-temperature additive. The relative density decreased slowly as the BCB content increased. The permittivity and $Q \times f$ values changed in a manner similar to the relative density, which decreased slightly as the BCB content increased from 0.5 to 3 wt%. The τ_f value decreased from -2 to -5 ppm/°C with increasing the addition of BCB because of negative τ_f value of BCB. For the 0.5 wt% BCB-added ceramic, a high relative density of 98.5% and good microwave dielectric properties of $\varepsilon_r = 26$, $Q \times f = 36{,}200$ (7.31 GHz) GHz and $\tau_f = -2$ ppm/°C has been obtained by sintering at 900 °C for 2 h.

For chemical compatibility tests with silver electrode, mixtures of ceramic powders with 20 wt% Ag powders were cofired and analyzed to detect interactions between the low-fired samples and electrodes. XRD patterns and backscattered electron image of $Li_2MgTi_3O_8$ ceramics added with 0.5 wt% BCB cofired with Ag at

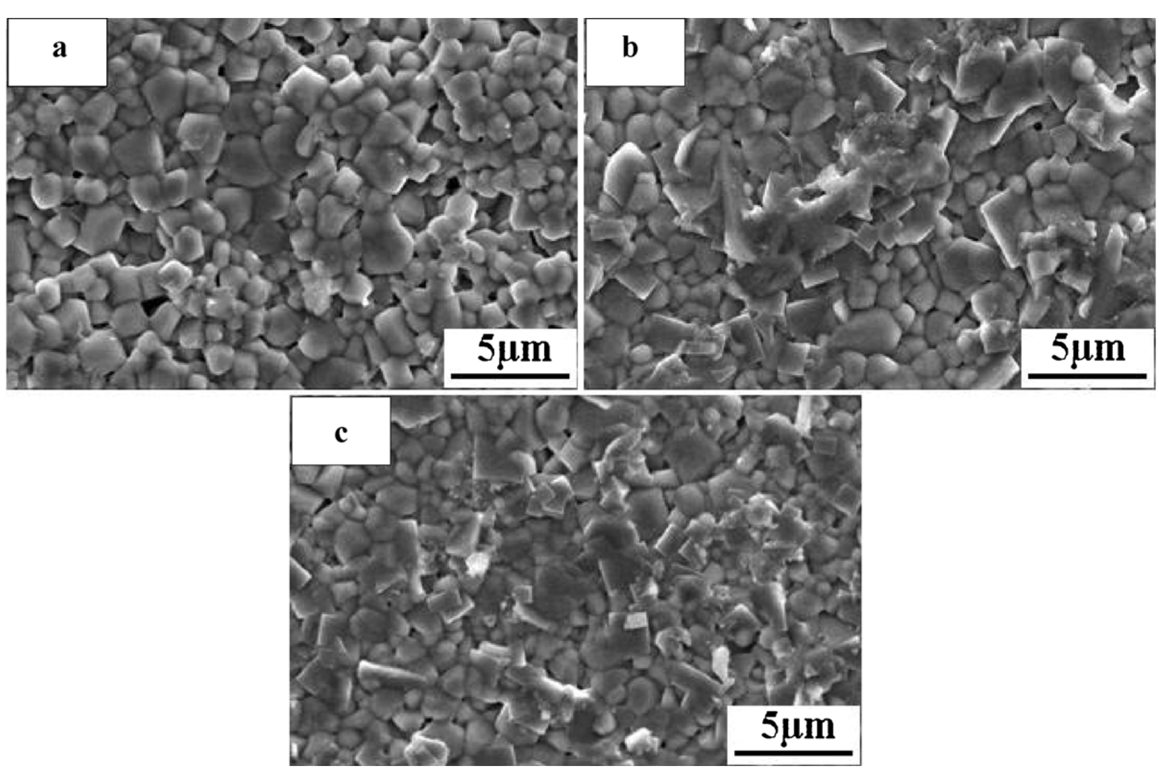

Fig. 5. SEM of BCB added $Li_2MgTi_3O_8$ powders sintered at 900 °C for 2 h: (a) 0.5 wt%, (b) 1.0 wt%, (c) 2.0 wt%.

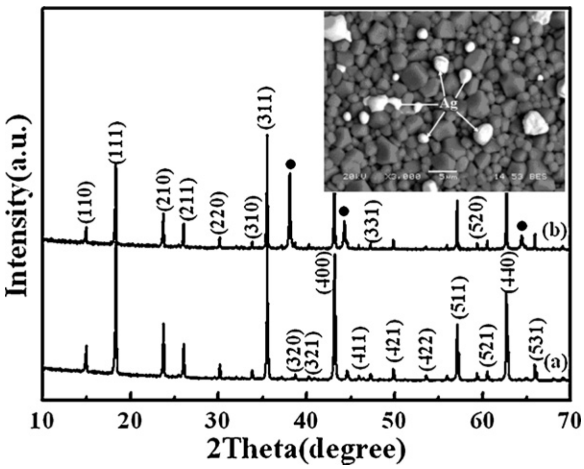

Fig. 7. Powder X-ray diffraction data collected for (a) $Li_2MgTi_3O_8$ ceramic sintered at 1025 °C, (b) 0.5 wt% BCB added samples mixed with 20 wt% Ag sintered at 900 °C. Inset shows backscattered electron image of 0.5 wt% BCB added $Li_2MgTi_3O_8$ samples cofired with Ag (•-Ag, JCPDS card #04-0783).

900 °C for 2 h are presented in Fig. 7. Backscattered electron image analysis reveals no interaction to form new phases after firing. This observation is also confirmed by the evidence of no difference between the XRD patterns before and after firing. It is obvious that the reaction of low-fired $Li_2MgTi_3O_8$ ceramics with Ag electrodes did not occur. Therefore, $Li_2MgTi_3O_8$ ceramics with BCB additives could be selected as a promising candidate for LTCC application because of low sintering temperature, good microwave dielectric properties, and chemical compatibility with Ag electrodes.

4. Conclusions

$Li_2MgTi_3O_8$ ceramic can be prepared by solid state reaction method and be well densified after sintering above 1025 °C for 2 h in air. The best microwave dielectric properties can be obtained in ceramic sintered at 1025 °C for 2 h with permittivity about 27.2, $Q \times f$ about 40 000 GHz and TCF about 2.6 ppm/°C. The addition of BCB can reduce the sintering temperature to 900 °C and induced only a limited degradation of the microwave dielectric properties. It is important that this material can co-fire with Ag electrodes. Obviously, the new kind of microwave dielectric ceramic is a suitable candidate for low temperature co-fired ceramics for applications in wireless communication system.

Acknowledgements

This work was supported by Natural Science Foundation of China (Nos. 50962004 and 50762002), Natural Science Foundation of Guangxi (Nos. 0832003Z and 0832001), and Program for NCET-06-0656, MOE, China, and Research start-up funds of Guilin University of Technology (Nos. 000788 and 000787).

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