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Microwave dielectric properties and compatibility with silver of low-fired $Li_2MgTi_3O_8$ ceramics with $Li_2O-MgO-B_2O_3$ frit

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Abstract: The effects of $Li_2O-MgO-B_2O_3$ (LMB) glass additive on the sintering characteristics, phase purity, microstructure, and microwave dielectric properties of $Li_2MgTi_3O_8$ ceramics were investigated. The experimental results demonstrate that the addition of LMB glass effectively lowers the sintering temperature of $Li_2MgTi_3O_8$ ceramic from 1025 °C to 875 °C and induces no obvious degradation of the microwave dielectric properties. Typically, the 1.5% LMB glass-added $Li_2MgTi_3O_8$ ceramic sintered at 875 °C for 4 h shows excellent microwave dielectric properties of $Q\times f$=45403 GHz, ε_r=25.9 and $\tau_f\approx0$ °C^{-1}. The dielectric ceramic exhibits stability against the reaction with the Ag electrode, which indicates that the ceramics could be applied in multilayer microwave devices requiring low firing temperatures.

Key words: microwave ceramics; dielectric properties; glass; low-temperature sintering; compatibility

1 Introduction

Recently, low temperature co-fired ceramic (LTCC) multilayer devices have been investigated to reduce the device size [1−6] to meet the demands of the miniaturization of microwave communication systems such as mobile systems. Silver has been widely used as the internal electrode in the multilayer devices because of its high conductivity and low cost [7−11]. The melting temperature of Ag is low. Therefore, for the fabrication of the multilayer devices, it is important to develop microwave dielectric ceramics that have low sintering temperatures and can be co-fired with Ag [12−14].

More recently, the microwave dielectric properties of $Li_2MgTi_3O_8$ ceramics have been investigated by GEORGE and SEBASTIAN [15]. They reported that this ceramic sintered at 1075 °C has good dielectric properties of relative permittivity ε_r=27.2, $Q\times f$=42000 GHz and resonant frequency τ_f=3.2×10^{-6} °C^{-1}. However, the sintering temperature of $Li_2MgTi_3O_8$ ceramic is too high to be applicable to LTCC. So, it is necessary to reduce the sintering temperature of this material. It is well known that the addition of a small amount of the lithium-based glass having very low melting temperature often makes it possible to decrease the sintering temperature of many microwave dielectric materials. For example, using 2.0% $Li_2O-ZnO-B_2O_3$ glass, the $ZnTiNb_2O_8$ dielectric can be sintered at 875 °C and obtain good microwave dielectric properties with ε_r=31.8, $Q\times f$=25.013 GHz and τ_f=−62×10^{-6} °C^{-1} [16]. GEORGE and SEBASTIAN [17] reported that the lithium magnesium zinc borosilicate glass-doped $Li_2MgTi_3O_8$ ceramic could be sintered at 925 °C, and showed the microwave dielectric properties of ε_r=24.5, $Q\times f$=44000 GHz, τ_f=0.2×10^{-6} °C^{-1}. Further investigations are still required for lowering its sintering temperature to less than 900 °C and enhancing the microwave dielectric properties so that they could be well co-fired with Ag electrode and improve the quality of devices.

In the present study, $Li_2O-MgO-B_2O_3$ (LMB) system glass was selected as the sintering aids. The LMB glass was chosen because the elements in the glass are Li and Mg, which are also present in the parent material ($Li_2MgTi_3O_8$). This may avoid the formation of secondary phase in the final product as far as possible

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[17]. LMB glass additive was made and added to $Li_2MgTi_3O_8$ ceramics in order to investigate the possibility using LMB as a low temperature sintering additive. Furthermore, its effect on the sintering behavior, microstructure and microwave dielectric properties of the $Li_2MgTi_3O_8$ ceramics was investigated. Meanwhile, the compatibility of the LMB glass-added ceramic with Ag electrode was also evaluated.

2 Experimental

Specimens of the $Li_2MgTi_3O_8$ ceramics were prepared by a conventional solid-state ceramic route from the high-purity oxide powders (>99.9%, Guo-Yao Co. Ltd., Shanghai, China) of Li_2CO_3, MgO and TiO_2. Stoichiometric amounts of the powder samples were mixed and ball milled using zirconia balls in ethanol medium for 24 h. The resultant slurry was then dried. The $Li_2MgTi_3O_8$ ceramic powders were calcined at 900 °C for 4 h. The LMB ($30Li_2O-10MgO-60B_2O_3$) glass was prepared from the high purity oxide chemicals of Li_2CO_3, MgO and H_3BO_3 (99.5%, Guo-Yao Co. Ltd., Shanghai, China). The glass batch filled in an uncovered corundum crucible was melted at 950 °C. The melt was homogenized for 1 h, then quenched and powdered. The glass softening point was 500 °C and the medium grain size of LMB glass powder was about 5 μm. After subsequent ball-milling of $Li_2MgTi_3O_8$ with 0−3.0% LMB, the powders were uniaxially pressed into disks of 12 mm in diameter and 6 mm in thickness under the pressure of about 100 MPa. The pure $Li_2MgTi_3O_8$ pellets were sintered at 1000−1100 °C for 4 h in air and the ceramic pellets added with LMB were sintered at 850−900 °C for 4 h in air.

The crystal structure and phase purity of the powdered samples were analyzed using X-ray diffraction (XRD, D8-ADVANCE, Bruker, Germany) with Cu K_α radiation. The bulk densities of the sintered samples were measured by the Archimedes method. The relative densities of various LMB doped $Li_2MgTi_3O_8$ samples were calculated using the bulk densities divided by their corresponding theoretical densities with the following formula [18]:

$$D = \frac{w_1 + w_2}{w_1 / D_1 + w_2 / D_2} \quad (1)$$

where w_1 and w_2 are the mass fractions of $Li_2MgTi_3O_8$ and LMB glass respectively; D_1 and D_2 are the theoretical densities of $Li_2MgTi_3O_8$ ceramic and LMB glass, respectively.

The microstructure observation of the samples was performed using scanning electron microscopy (SEM, JEOL JSM−5610LV, Tokyo, Japan). The microwave dielectric properties were measured by a Vector Network Analyzer (N5230C, Agilent Technologies) [19]. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range of 25−75 °C using the following equation:

$$\tau_f=(f_{75}-f_{25})/(50\times f_{25}) \quad (2)$$

where f_{75} and f_{25} are the resonant frequencies at 75 °C and 25 °C, respectively.

To check the chemical compatibility of the ceramic with the silver powder, 20% powdered silver was mixed and homogenized with the 1% LMB glass-added $Li_2MgTi_3O_8$ ceramic powder [20], and then the mixture was pressed into pellets and fired at 875 °C for 4 h to achieve equilibrium. In addition to the XRD analysis, micro-structural study and line scan were conducted via scanning electron microscopy (SEM, JSM−5610, JEOL, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS).

3 Results and discussion

The room-temperature XRD patterns recorded for the pure $Li_2MgTi_3O_8$ ceramic sintered at 1025 °C for 4 h are shown in Fig. 1. All the diffraction peaks of the ceramic sample could be indexed as a cubic structure (*P*4332) $Li_2MgTi_3O_8$ (PDF 89—1308) without any secondary phase, which agreed well with those reported by KAWAI et al [21]. The theoretical density of the $Li_2MgTi_3O_8$ ceramic calculated from XRD data is about 3.50 g/cm^3 [15]. The SEM image 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 4 h with only few pores existing can be confirmed by SEM.

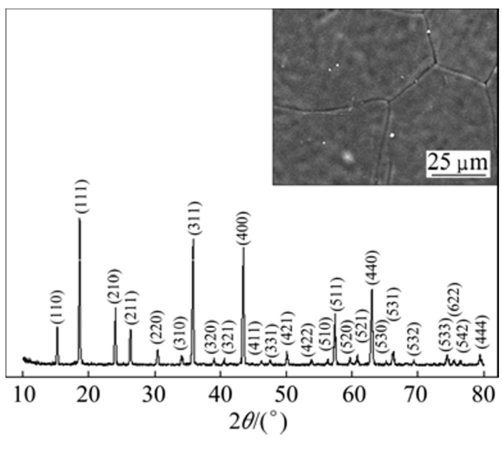

Fig. 1 XRD pattern of $Li_2MgTi_3O_8$ ceramic sample sintered at 1025 °C for 4 h (Inset shows SEM image of as-sintered $Li_2MgTi_3O_8$ sample)

Figure 2 presents the bulk densities and relative densities of $Li_2MgTi_3O_8$ ceramics as a function of