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Short communication

Microwave dielectric properties and chemical compatibility with silver electrode of low-fired $Li_2Cu_{0.2}Mg_{0.8}Ti_3O_8$ ceramic

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Abstract

A new high-Q, low-temperature microwave dielectric ceramic with composition $Li_2Cu_{0.2}Mg_{0.8}Ti_3O_8$ and a cubic spinel structure was prepared at 900–975 °C for 2 h by the conventional solid-state route. The ceramic sintered at 950 °C for 2 h exhibits optimum dielectric properties with a moderate dielectric constant of 28.1, a high quality factor of 34,300 GHz and a near-zero temperature coefficient of resonance frequency of 9.4 ppm/°C. The $Li_2Cu_{0.2}Mg_{0.8}Ti_3O_8$ ceramic can be compatible with Ag electrode, which makes it a promising ceramic for LTCC technology application.

Keywords: A. Sintering; C. Dielectric properties; D. Spinels; E. Functional applications

1. Introduction

In the past decades, along with the rapid progress in wireless and mobile communications, a number of microwave devices such as filters, duplexers, resonators and antennas were well developed [1]. Modern electronic devices tend to be miniature and portable, thus it requires the related electronic components to be highly integrative and with high performance. Low-temperature co-fired ceramic (LTCC) technology makes it possible to integrate many kinds of electronic components and devices in a compact multilayer ceramic structure, fulfilling the demands [2]. To realize co-firing with Ag electrode, the sintering temperature of these ceramic materials should be lower than 960 °C [3]. Unfortunately, many commercial microwave dielectric ceramics such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $CaTiO_3$–$NdAlO_3$, BaO–Nd_2O_3–TiO_2 usually have a high sintering temperature (>1300 °C), which cannot be directly applied as LTCC [4]. At the same time, some low sintering materials, such as TeO_2-rich compounds, Bi_2O_3-rich compounds, MoO_3-rich compounds, have a sintering temperature below 960 °C, but they are reactive with Ag electrode and hence not suitable for application as LTCC [5–11]. Therefore, it is necessary to reduce the sintering temperature of the ceramics which have chemical compatibility with the Ag electrodes.

Recently, Li-containing microwave dielectric ceramics have attracted much attention due to its low sintering temperature and environmental-friendly, like Li2TiO3, $Li_{3-3x}M_{4x}Nb_{1-x}O_4$ (M=Mg, Zn) [12], Li_2MgSiO_4 [13] and so on. Li-based spinels, such as $Li_2MTi_3O_8$ (A=Zn, Mg, Co), $Li_2M_3Ti_4O_{12}$ (M=Co, Zn, Mg) [14–19], were reported to be well sintered in the temperature range of 1050–1125 °C, and exhibited good microwave dielectric properties with dielectric constant (ε_r) in the range 20–29, high quality factor ($Q\times f$) value up to 106,000 GHz and low temperature coefficient of resonance frequency (τ_f) in the range of −48–7.4 ppm/°C. Among them, George and Sebastian firstly reported $Li_2MgTi_3O_8$ with a good microwave dielectric properties of $\varepsilon_r=27.2$, $Q\times f=42{,}000$ GHz and $\tau_f=3.2$ ppm/°C. However, the sintering temperature (~1075 °C) is still too high to be applicable to the LTCC technology.

Considering the Shannon's effective ionic radius of Cu^{2+} (0.745 Å) is very close to that of Mg^{2+}(0.72 Å) [20], and Cu substitution for Mg in Mg–Zn ferrites [21]

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and $Yb_2Ba(Cu_{1-x}M_x)O_5$ (M = Zn, Ni) [22] ceramics have been reported to effectively reduce their sintering temperatures and adjust dielectric properties, then Cu substitution for Mg^{2+} in the $Li_2MgTi_3O_8$ system might explore new materials to meet the requirement of LTCC. Therefore, we have carried out the research to prepare and characterize the dielectric properties of $Li_2Cu_xMg_{1-x}Ti_3O_8$ (x = 0–0.5) system, and found that the τ_f gradually increased from 3.2 ppm/°C to 48.1 ppm/°C while the ε_r increased from 27.2 to 28.6 and $Q \times f$ decreased from 42,000 GHz to 9100 GHz as x increased. In the present work, a new low-firing and low loss microwave dielectric ceramic $Li_2Cu_{0.2}Mg_{0.8}Ti_3O_8$ with near-zero τ_f was obtained, and its sintering behavior, microwave dielectric properties and chemical compatibility with silver were reported.

2. Experimental procedure

High-purity powders of Li_2CO_3 (≥ 98.0%), MgO (≥ 99.0%), CuO (≥ 99.0%) and TiO_2 (≥ 99.99%) were mixed according to the composition of $Li_2Cu_{0.2}Mg_{0.8}Ti_3O_8$. The mixed oxides were ball-milled in a polyethylene bottle with zirconia media for 4 h using alcohol as a medium. The wet mixtures were rapidly dried and calcined at 750 °C for 4 h. The calcined powders were milled for 6 h, then the slurry was dried and ground well. Polyvinyl alcohol (PVA, 5 wt%) was added to the powders as binder. The powders were then pressed into cylinders with 12 mm in diameter and 6–7 mm in height by uniaxial pressing under a pressure of 200 MPa. The samples were heated to 550 °C for 4 h to remove the organic binder and then sintered at 900–975 °C for 4 h.

The phase composition of samples was analyzed using an X-ray diffractometer (CuKα_1, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Netherlands). The apparent densities of the sintered samples were measured by the Archimedes method. The surface microstructure of the samples was examined using a scanning electron microscopy (JSM6380-LV, JEOL, Tokyo, Japan). The microwave dielectric properties were analyzed using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficient of resonant frequency (τ_f) was measured in a temperature range from 25 °C to 85 °C. The τ_f values were calculated by the formula as follows:

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

where f_T, f_0 were the resonant frequencies at the measuring temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

The room temperature XRD patterns recorded for the $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ sintered at 900–975 °C using CuKα radiation are shown in Fig. 1. These patterns are similar and match well with PDF files No. 01-089-1308 of $Li_2MgTi_3O_8$. All the peaks could be well indexed and there was no evidence of any secondary phases present. The $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ crystallizes in a cubic spinel structure with space group $P4_332$, and the single phase is easily formed since the Mg^{2+} and Cu^{2+} are isovalent, and Shannon's effective ionic radii are similar (0.72 Å for Mg^{2+} and 0.745 Å for Cu^{2+}) [20].

Fig. 2 shows the SEM micrographs for $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics sintered in the range of 900∼975 °C for 4 h. The grain size of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics increases with increasing sintering temperatures. For the specimen sintered at 900 °C, the microstructure is observed with few pores, and most of the grains are small, approximately 3–5 μm. A well-sintered and uniform microstructure with grain sizes in the range 5–7 μm can be achieved at 950 °C. The grain size was increased as the sintering temperature increases from 925 °C to 950 °C. And abnormal grain growth occurs as the sintering temperature exceeds 975 °C. A few large grains with size over 40 μm and a small amount of pores at the grains are observed in Fig. 2(d).

Fig. 3 presents the relative density and the microwave dielectric properties of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics sintered at different temperatures from 900 to 975 °C. The relative density of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramic increased with increasing sintering temperature, reached a maximum value (96.3%) as the sintering temperature was 950 °C, and then decreased slightly which might be attributed to the volatilization of lithium and abnormal grain growth [23]. Microwave dielectric properties versus sintering temperature of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics exhibited a trend similar to that of the relative density. As the sintering temperature increases, ε_r increases from 26.8 to 28.1, $Q \times f$ enhances from 29 800 GHz to 34 300 GHz, and τ_f gradually improves from 12.7 to 9.4 ppm/°C. The value of ε_r primarily depended on the composition, grain size and the density. The density of the samples affected ε_r markedly. The $Q \times f$ value is mainly affected by the densification of the ceramics. The improvements in $Q_u \times f$ can also be attributed to the increase of densification. On the other hand, the deterioration of $Q_u \times f$ might be due to

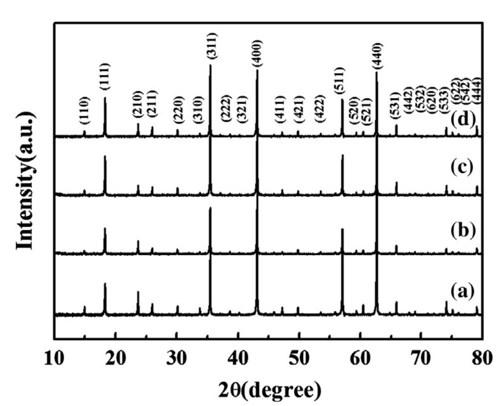

Fig. 1. XRD patterns of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ sintered at different sintered temperature: (a) 900 °C; (b) 925 °C; (c) 950 °C and (d) 975 °C.

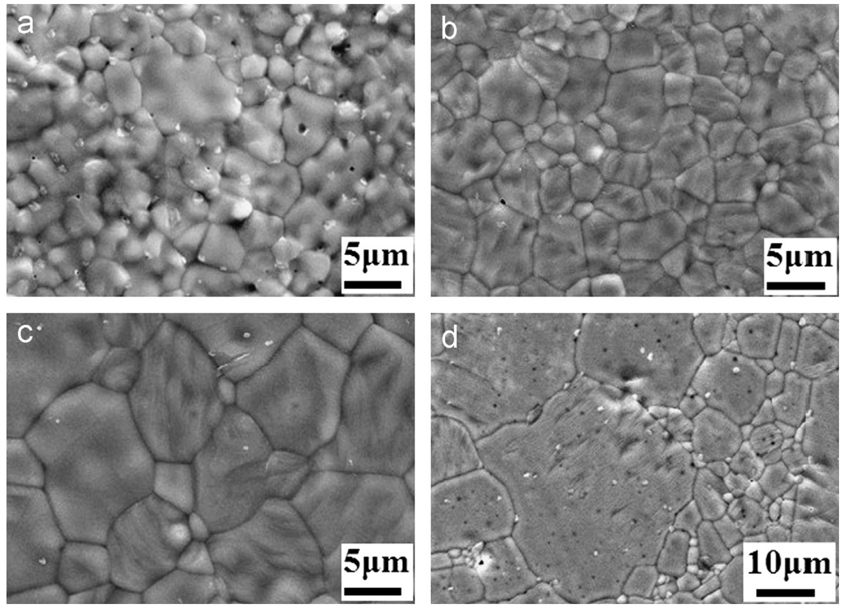

Fig. 2. SEM micrographs for $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics sintered at different temperature: (a) 900 °C; (b) 925 °C; (c) 950 °C and (d) 975 °C.

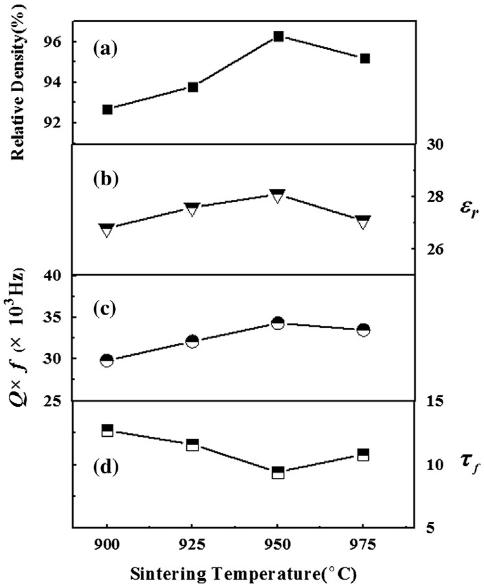

Fig. 3. Variations of (a) relative densities, (b) ε_r, (c) $Q \times f$, and (d) τ_f of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics at different sintering temperature.

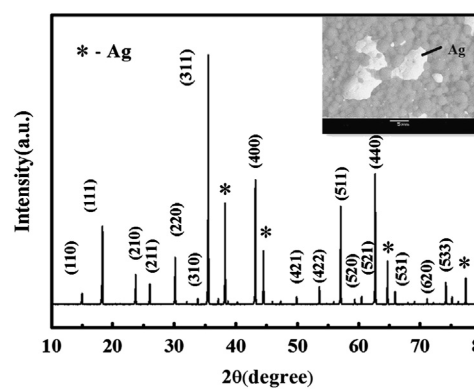

Fig. 4. XRD patterns of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics mixed with 20 wt% Ag sintered at 950 °C for 2 h. Insert shows a backscattered electron image of $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ samples cofired with Ag.

the decreased densification caused by the evaporation of lithium at elevated temperatures [24–27].

Since $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramic exhibits a low sintering temperature (~950 °C), good microwave dielectric properties ($\varepsilon_r = 28.1$, $Q \times f = 34{,}300$ GHz, $\tau_f = 9.4$ ppm/°C), low bulk density (< 4 g/cm^3) and low cost (cheap raw materials), then it is necessary to evaluate the chemical compatibility of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramic with silver electrode for LTCC application. XRD patterns and backscattered electron image of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ cofired with 20 wt% Ag powders at 950 °C for 2 h are presented in Fig. 4. Since the XRD pattern of $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$/Ag sample does not show any other phase and the backscattered electron image of the mixtures does not create new phases after sintering. So, there is no reaction between low-fired $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramics and Ag electrodes. Therefore, $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ could be a suitable candidate for LTCC materials, because of low sintering temperature, good microwave dielectric properties, and chemical compatibility with Ag electrodes.

4. Conclusion

The $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramic with cubic spinel structure has been prepared by the conventional solid-state ceramic reaction method. Cu substituted for Mg can effectively lower the sintering temperatures of the ceramics and significantly affect the dielectric properties. $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ ceramic sintered at 950 °C/2 h exhibits the best combination of microwave dielectric properties with ε_r of 28.1, $Q\times f$ of 34,300 GHz and τ_f of 9.4 ppm/°C. The backscattered electron image and XRD analysis shows ceramic can co-fire with Ag electrodes. Obviously, $Li_2Mg_{0.8}Cu_{0.2}Ti_3O_8$ might be an attractive promising candidate for LTCC application in the wireless communication system.

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