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Letter

Low-temperature sintering and microwave dielectric properties of Li_3MO_4 (M = Ta, Sb) ceramics

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ABSTRACT

Both Li_3TaO_4 and Li_3SbO_4 ceramics were prepared via the solid state reaction method. With 1 wt.% B_2O_3 addition, the sintering temperatures of both Li_3TaO_4 and Li_3SbO_4 ceramics can be lowered to near 930 °C. The chemical compatibility of silver electrode and the low-firing ceramics has been considered, and the results showed that both the Li_3TaO_4 and Li_3SbO_4 ceramics are chemical compatible with Ag. Good microwave dielectric properties were obtained with permittivities of 14.1 and 10.3, quality factor Q_f values of 29,900 (at 12.4 GHz) and 14,600 GHz (at 13.5 GHz), and temperature coefficient of resonant frequency values of −48 and −28 ppm/°C for Li_3TaO_4 and Li_3SbO_4 ceramics with 1 wt.% B_2O_3 addition, respectively.

1. Introduction

Low temperature co-fired ceramic (LTCC) technology has been critically important in the development of electronic devices for wireless communication. Transition from surface mount discrete components to integrated components in a substrate requires LTCC materials which can be co-fired with metal electrodes. In order to use the most common electrode silver, ceramic must have low sintering temperature below 960 °C and chemical compatibility with Ag [1–9].

Our previous work showed that Li_3NbO_4 ceramic is a promising dielectric material for LTCC technology with permittivity (ε_r) of 15.8, Q_f value of 55,009 GHz and temperature coefficient of resonant frequency (TCF) about −49 ppm/°C [10]. Most of time, Ta^{5+} and Sb^{5+} ions have similar chemical and physical properties with Nb^{5+}, and they could be submitted by each other in the compounds [11,12]. In this work, the sintering behavior and microwave dielectric properties of Li_3MO_4 (M = Ta, Sb) ceramics were studied. The sintering adds B_2O_3 [13] was used to improve the sintering behavior of Li_3MO_4 (M = Ta, Sb) ceramics and to get materials for LTCC application.

2. Experimental

Proportionate amounts of reagent-grade starting materials of Li_2CO_3, Ta_2O_5, and Sb_2O_3 (>99%, Guo-Yao Co. Ltd., Shanghai, China) were prepared according to the composition Li_3MO_4 (M = Ta, Sb). The raw materials were mixed and milled for 4 h. Powders were then calcined at 900 °C for 4 h and re-milled for 5 h with *x* wt.% B_2O_3 addition (*x* = 0.0, 1.0). The final Green cylinder samples were sintered at temperature 1100–1230 °C or 870–990 °C for 2 h.

To check the chemical compatibility of the low-fired Li_3TaO_4 and Li_3SbO_4 ceramics with the silver electrode, 20 wt.% powdered silver was mixed and homogenized with the ceramic powder [14], and then the mixture was pressed into pellets and fired at 930 °C for 2 h to achieve equilibrium.

The crystalline structures of samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan) using ground powders. The apparent densities of sintered ceramics were measured by Archimedes' method. Dielectric behaviors at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The temperature coefficient of resonant frequency (TCF) was calculated by the following formula:

$$\mathrm{TCF} = \frac{f_{85} - f_{25}}{f_{85} \times (85 - 25)}\ (\mathrm{ppm/^{\circ}C}) \qquad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the apparent density of Li_3MO_4 (M = Ta, Sb) ceramics vs. sintering temperature. The pure Li_3MO_4 (M = Ta, Sb) ceramics were difficult to be well densified and their sintering temperatures were relatively high (above 1200 °C). To lower the sintering temperature, B_2O_3 was used as the sintering additive. As seen in Fig. 1, with 1 wt.% B_2O_3 addition, the apparent densities of both Li_3TaO_4 and Li_3SbO_4 ceramics got saturated values after being sintered at 900 °C. It means that the sintering temperatures of Li_3MO_4 (M = Ta, Sb) ceramics was lowered to about 900 °C, and this sintering temperature makes it possible for use in LTCC technology.

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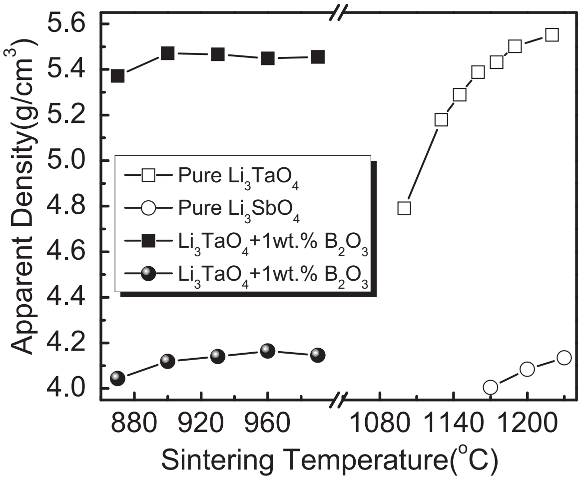

Fig. 1. Apparent density of Li_3MO_4 (M = Ta, Sb) ceramics as a function of sintering temperature.

The XRD patterns of Li_3MO_4 (M = Ta, Sb) samples calcined at 900 °C for 4 h and the co-fired ceramics with 20 wt.% Ag powders sintered at 930 °C for 2 h are shown in Fig. 2. It can be seen that pure phase can be obtained in both of the calcined Li_3TaO_4 and Li_3SbO_4 samples. The diffraction peaks of Li_3TaO_4 sample can be indexed as a rock salt-type monoclinic structure with space group *C*2/*c* (15), which agrees well with Zocchi et al.'s report [15]. The Li_3SbO_4 belongs to a monoclinic structure with space group P2/c (13) as reported by Skakle et al. [16]. From the XRD patterns of the co-fired samples, it can be seen that only Li_3MO_4 (M = Ta, Sb) phase and cubic Ag phase were observed, which indicates that both the Li_3TaO_4 and Li_3SbO_4 ceramics are chemical compatible with silver at a sintering temperature of 930 °C.

The microwave dielectric properties of Li_3MO_4 (M = Ta, Sb) ceramics as a function of sintering temperature are shown in Fig. 3, and Table 1 presents their best microwave dielectric properties and the corresponding sintering temperatures. Both the dielectric constant (permittivity) and Q_f value of pure Li_3MO_4 (M = Ta, Sb) ceramics are sensitive with the sintering temperature, as shown in Fig. 3. For Li_3TaO_4, the best microwave dielectric properties were obtained in ceramic sintered at 1160 °C for 2 h with permittivity of 13.9, Q_f value about 35,300 GHz, and its TCF value was −52 ppm/°C (as listed in Table 1). The pure Li_3SbO_4 ceramic sintered at 1200 °C possesses relatively much lower permittivity of 7.7, Q_f value of 16,400 GHz, and TCF value of −45 ppm/°C. As shown in Fig. 3, the microwave dielectric properties of Li_3MO_4 (M = Ta, Sb) ceramics with 1 wt.% B_2O_3 addition were much stable with the changed sintering temperature in the range of 900–960 °C. The Li_3TaO_4 ceramic with 1 wt.% B_2O_3 addition shows microwave dielectric properties with permittivity of 14.1, Q_f value of 29,900 GHz, and TCF value of −48 ppm/°C. For Li_3SbO_4 ceramic with 1 wt.% B_2O_3 addition, its dielectric constant, Q_f value, and TCF value are 10.3, 14,600 GHz, and −28 ppm/°C, respectively. Compared with the case of Li_3NbO_4 ceramic, both pure Li_3TaO_4 and Li_3SbO_4 ceramics have much higher sintering temperatures. The addition of 1 wt.% B_2O_3 effectively lowered the sintering temperature to near 930 °C without much deterioration of Q_f values as listed in Table 1. Comparing with other commonly used low-permittivity LTCC materials of multiphase, such as Al_2O_3, MO—SiO_2 (M = Ca, Mg, Zn), MO—TiO_2, and $CaWO_4$ based ceramics or glass–ceramic [17–20], the Li_3MO_4 (M = Ta, Sb) ceramics with 1 wt.% B_2O_3 addition possessed comparative microwave dielectric properties (as shown in Table 1), and crystallized as a single phase ceramic, which would be beneficial to the property of mechanical strength and repeatability of a LTCC substrate material.

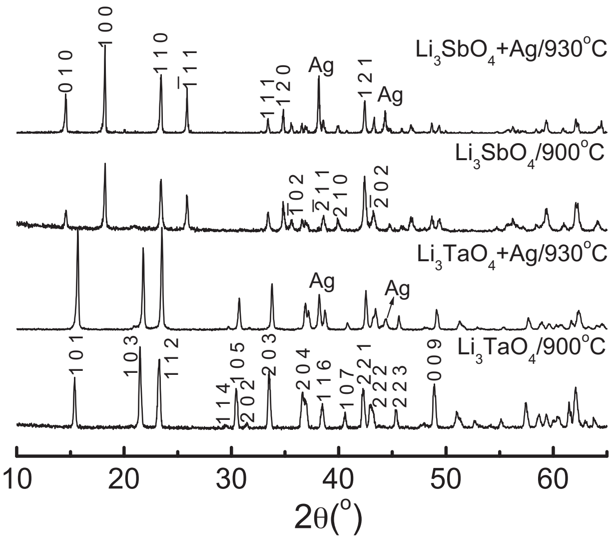

Fig. 2. XRD patterns of Li_3MO_4 (M = Ta, Sb) samples calcined at 900 °C for 4 h and the co-fired samples with 20 wt.% Ag powders sintered at 930 °C for 2 h.

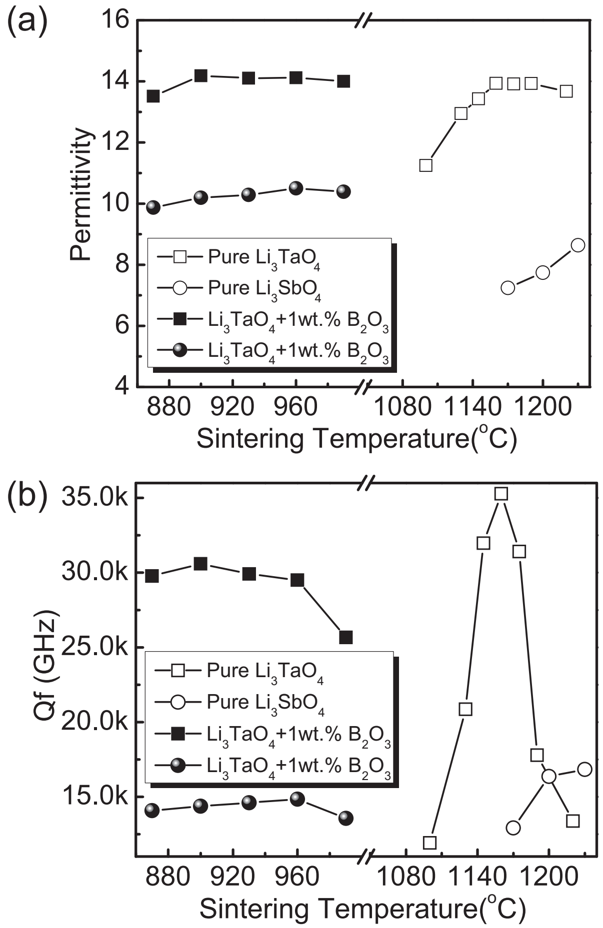

Fig. 3. Microwave dielectric constant (a) and Q_f value (b) of Li_3MO_4 (M = Ta, Sb) ceramics as a function of sintering temperature.

Table 1
Microwave dielectric behavior of Li_3MO_4 (M = Ta, Sb, Nb) ceramics and other low-permittivity LTCC materials.

Sample	S.T. (°C)	Frequency (GHz)	Permittivity	Q_f (GHz)	TCF (ppm/°C)
Li_3TaO_4	1160	9.42	13.9	35,300	−52
Li_3SbO_4	1200	12.20	7.7	16,400	−45
Li_3TaO_4, $w(B_2O_3) = 1.0\%$	930	12.40	14.1	29,900	−48
Li_3SbO_4, $w(B_2O_3) = 1.0\%$	930	13.46	10.3	14,600	−28
Li_3NbO_4 [10]	930	8.99	15.8	55,009	−49
$w(Al_2O_3) = 50\%$, $w(ZnO—B_2O_3—SiO_2) = 50\%$ [17]	900		5.72	17,757	−21
$(Zn_{0.8}Mg_{0.2})_2SiO_4—TiO_2$, $w(Li_2O—B_2O_3—SiO_2) = 3\%$ [18]	870		8.48	11,500	0
$0.85CaWO_4—0.15SmNbO_4$, $w(Li_2MoO_4) = 1\%$ [19]	800		12.03	11,300	−28.6
$MgTiO_3—CaTiO_3$, $ZnO—B_2O_3—SiO_2$ [20]	900		8.5	8889	6.2

S.T.: sintering temperature.

4. Conclusions

Both pure Li_3TaO_4 and Li_3SbO_4 phases can be formed at 900 °C. The addition of 1 wt.% B_2O_3 can effectively lower the sintering temperatures of both Li_3TaO_4 and Li_3SbO_4 ceramics to near 930 °C. The Li_3TaO_4 ceramic with 1 wt.% B_2O_3 addition shows microwave dielectric properties with a permittivity of 14.1, a Q_f value of 29,900 GHz, and TCF value of −48 ppm/°C at frequency 12.4 GHz. For Li_3SbO_4 ceramic with 1 wt.% B_2O_3 addition, its dielectric constant, Q_f value, and TCF value are 10.3, 14,600 GHz (at 13.5 GHz), and −28 ppm/°C, respectively. The XRD results of co-fired sample show that both the Li_3TaO_4 and Li_3SbO_4 ceramics are chemical compatible with Ag at 930 °C.

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