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Microwave dielectric properties of low-fired Li_2SnO_3 ceramics co-doped with MgO–LiF

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ABSTRACT

Low-fired Li_2SnO_3 ceramics co-doped with MgO–LiF were fabricated by a conventional solid-state route, and their sinterability, microwave dielectric properties were investigated. With increasing MgO content, a novel phase $Li_2Mg_3SnO_6$ was formed. A near-zero τ_f value was obtained at 1325 °C for Li_2SnO_3-8 wt% MgO ceramics. Furthermore, LiF addition not only successfully lowered the sintering temperatures to 880 °C but also promoted formation of $Li_2Mg_3SnO_6$. The microwave dielectric properties of Li_2SnO_3-8 wt% MgO ceramics were further optimized with increasing $Li_2Mg_3SnO_6$ content. The excellent microwave dielectric properties ($\varepsilon_r = 14.7$, $Q \times f = 78{,}400$ GHz, and $\tau_f = -0.9$ ppm/°C) were achieved at 880 °C for Li_2SnO_3-8 wt% MgO-2 wt% LiF ceramics, which is compatible with Ag electrodes and suitable for the low-temperature co-fired ceramics (LTCC) applications.

1. Introduction

With developing wireless and mobile communication industry, microwave dielectric ceramics have been widely used in fields such as telecommunication, radar and navigation. Nowadays, the low-temperature co-fired ceramic (LTCC) multilayer devices are very attractive subjects due to their alternating compact of dielectric ceramic substrates and internal metallic electrode layers. Four characteristic properties are required for LTCC applications [1]: appropriate dielectric constant ($\varepsilon_r \leq 25$) to avoid signal delay, high quality factor ($Q \times f \geq 5000$ GHz) for selectivity, a near-zero temperature coefficient of resonant frequency ($|\tau_f| \leq 10$ ppm/°C) for stability, lower sintering temperature (Ts < 960 °C) and excellent chemical compatibility with the Ag electrode. Several methods have been developed for this purpose: using ultrafine nanopowders as raw materials [2], searching for new ideal low-temperature sintered ceramic material [3], or adding sintering aids into dielectric ceramic systems [4]. Among them, adding sintering aids is the most effective and cheapest method to improve the sinterability of ceramics.

Recently, lithium based oxide ceramics Li_2MO_3 (M = Sn, Ti, Zr), Li_3MO_4 (M = Sb, Ta), and $Li_2ATi_3O_8$ (A = Mg, Zn) have aroused considerable attention from materials research and engineering applications [5–7]. Among them, Li_2TiO_3 ceramic with rock salt structure received special attention due to its good dielectric properties: $\varepsilon_r \simeq 19$, $Q \times f$ above 23,600 GHz, and $\tau_f = 38$ ppm/°C [5]. However, its Ts (around 1200 °C) are too high to be applied in LTCC and τ_f value is a little large. A near-zero τ_f value was obtained by forming a solid solution with MgO or ZnO [8,9]. By adding glass frits such as H_3BO_3, Li_2O–MgO–B_2O_3 or ZnO–B_2O_3, the densification temperatures were reduced to 850–950 °C [10–12]. But the glassy phase is detrimental to enhancing dielectric properties due to higher dielectric loss. Li_2SnO_3 has the similar rock salt structure with Li_2TiO_3 [13]. Its τ_f value was modified and $Q \times f$ values were improved by compositing with MgO, ZnO or Li_3NbO_4 [14,15]. However, the higher sintering temperatures (1200–1325 °C) and porous microstructure of Li_2SnO_3 based ceramics hindered their practical applications. Low melting fluorides (such as LiF, CaO–B_2O_3) were reported to be effective as sintering flux in several microwave ceramic systems [16–19].

In this work, we used MgO as an t_f compensator and LiF as sintering aid for Li_2SnO_3 ceramics. The effects of MgO and LiF on the structural evolution, sintering characteristics, microstructures and microwave dielectric properties of Li_2SnO_3 ceramics were studied systematically.

2. Experimental procedure

Li_2SnO_3 ceramics doped with (2–13 wt%) MgO and (0–6 wt%) LiF were prepared by the conventional solid-state route. Li_2CO_3 (98%),

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SnO_2 (99.5%), MgO (99.99%) and LiF (99.6%) powders were used as starting materials. Stoichiometric Li_2CO_3 and SnO_2 were mixed according to the formula of Li_2SnO_3 and milled with ZrO_2 balls in ethanol for 8 h. Then the mixtures were dried and calcined at 700 °C for 4 h in air. The obtained Li_2SnO_3, MgO and LiF powders were weighed according to the designed molar ratios, ball-milled for 8 h, dried and sieved. Subsequently, the powders were granulated with 5 wt% PVA as binder and uniaxially pressed into cylindrical disks (11.5 mm in diameter and about 6 mm in height) under a pressure of 98 MPa. These pellets were sintered at 840–1350 °C for 6 h on alumina plates at a heating rate of 4 °C/min.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structures were analyzed using X-ray diffraction (XRD) with Cu$K\alpha$ radiation (Rigaku D/MAX2550, Tokyo, Japan). The Raman spectra were excited with the 532 nm line of a semiconductor laser at a power of 250 mW and recorded in back-scattering geometry using InVia Raman Microscope equipped with a grating filter. The microstructures were investigated using a scanning electron microscope (SEM, Quanta 200, FEI Company, Eindhoven, Holland) coupled with energy dispersive X-ray spectroscopy (EDS). The microwave dielectric properties of the specimens were measured using a network analyzer (ZVB20, Rohde & Schwarz, Munich, Germany) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient resonant frequency (τ_f) was calculated with the following formula:

$$\tau_f = \frac{(f_2 - f_1) \times 10^6}{f_1 (T_2 - T_1)} \tag{1}$$

where, f_2 and f_1 represent the resonant frequency at T_2 and T_1, respectively.

3. Results and discussion

3.1. Li_2SnO_3 doped with MgO system

Fig. 1 shows the XRD patterns of (0–13) wt% MgO doped Li_2SnO_3 ceramics sintered at different temperatures. The XRD patterns displayed pure Li_2SnO_3 phase (PDF# 31-0761) for the samples doped with (0–2) wt% MgO. With increasing MgO content more than 5 wt%, a novel phase of $Li_2Mg_3SnO_6$ (PDF# 39-0932) was observed accompanied by a reduction of Li_2SnO_3 phase, which is in agreement with reported [20]. This means that the following reaction occurs:

$$Li_2SnO_3 + 3MgO \rightarrow Li_2Mg_3SnO_6 \tag{2}$$

Our results are different from the reported [14], where mixtures of $Li_4MgSn_2O_7$ and Li_2SnO_3 phases were observed in Li_2SnO_3–MgO ceramics. However, our XRD results unambiguously demonstrated the existence of $Li_2Mg_3SnO_6$ indicated by the presence of $2\theta = 42.35°$ reflection peak and will be further evidenced by XRD and EDS analysis later.

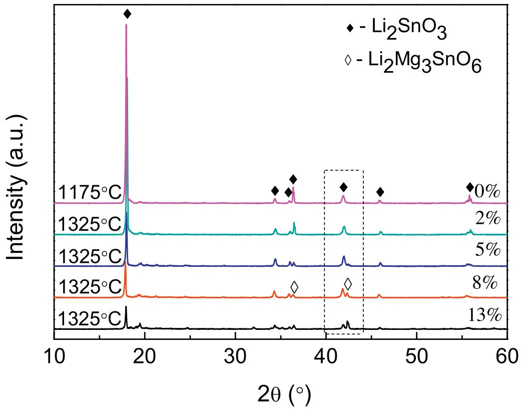

Fig. 1. XRD patterns of Li_2SnO_3 ceramics doped with (0–13) wt% MgO.

The SEM images of (0–13) wt% MgO doped Li_2SnO_3 ceramics sintered at various temperatures are shown in Fig. 2. The sintered samples exhibited porous microstructure. Compared with pure Li_2SnO_3 ceramics, the MgO-doped samples displayed larger porosity, similar phenomenon were observed in Li_2TiO_3–MgO system [9]. The higher porosity of Li_2SnO_3 based ceramics was partly due to the volatilization of Li of high temperature, accompanying with weight loss up to ≥6 wt% (Fig. 2(f)), and partly ascribed to the rapid coalescence of small subgrains which lead to the pore isolation in the large grains because of boundary breakaway [14]. The highly preferred orientation plate-like grain structures were also observed in MgO-doped samples. Table 1 presents bulk densities and microwave dielectric properties of MgO-doped Li_2SnO_3 ceramics sintered at optimum temperatures. With increasing MgO content, bulk density and dielectric permittivity decreased due to lighter weight and lower ε_r value (9.7) of MgO. It is noteworthy that MgO addition improved $Q \times f$ and frequency–temperature stability. Well dielectric properties of $\varepsilon_r \simeq 13.2$, $Q \times f \simeq 57{,}000$ GHz, and $\tau_f = -0.0$ ppm/°C was obtained at 1325 °C for Li_2SnO_3-8 wt% MgO (LSM) ceramics.

3.2. Li_2SnO_3-8 wt% MgO doped with LiF system

In order to decrease the sintering temperature lower than 950 °C for LTCC applications, LiF powders were added into LSM matrix. Fig. 3 illustrates the XRD patterns of $x$wt% ($0 \leq x \leq 6$) LiF doped LSM ceramics sintered at different temperatures. The XRD patterns exhibited a two-phase system with a monoclinic Li_2SnO_3 and a cubic $Li_2Mg_3SnO_6$ phase. The amount of $Li_2Mg_3SnO_6$ phase increased with increasing LiF content (x). Furthermore, the peaks of $2\theta = 18°$ shifted toward higher angle then back toward lower ones with increasing LiF content, which implied lattice contraction and lattice expansion. Table 2 displays the variation in lattice constant of Li_2SnO_3 ceramics with increasing LiF content. The lattice contraction might be owing to the substitution of the F^- ion ($R = 1.33$ Å) in the O^{2-} ($R = 1.4$ Å) sites, the similar phenomenon was observed in Li_2TiO_3–LiF system [16]. The replacement mechanisms as following:

$$3LiF \xrightarrow{Li_2SnO_3} Li'''_{Sn} + 3F^{\bullet}_{O} + 2Li^{\times}_{Li} \tag{3}$$

While LiF addition $x \geq 6$ wt%, the increase of lattice constant was associated with a large extent of liquid phase during sintering process inhibit the entrance or occupation of Li^+ and F^- in the Li_2SnO_3 lattice.

The Raman spectra of LSM-$x$wt% LiF ceramics sintered at different temperatures are given in Fig. 4. The spectra of $x \geq 1$ samples were similar to that of pure LSM, which exhibited several first order Raman active modes at 242 cm^{-1}, 369 cm^{-1} and 591 cm^{-1}. The width of the mode increased with increasing x implying that the arrangement of atoms in crystal became more disorderly, in agreement with the reported [21,22]. A new broad band near 650 cm^{-1}, which was considered to associate with $Li_2Mg_3SnO_6$ phase (its Raman spectra is given in insert of Fig. 4), was observed with increasing LiF content.

Addition of LiF as sintering aid in the LSM ceramics can bring about two effects during the sintering process. On one hand, liquid phase can be formed during the sintering because of lower melting point of LiF (845 °C), which could enhance grain boundary mass transport significantly. On the other hand, the substitution of smaller F^- for O^{2-} would cause weakening of oxygen bond strength which reduces the intrinsic sintering temperature and facilitates the diffusion process [22]. The SEM images of LSM-$x$wt% LiF