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Original Article

A new Li-based ceramic of $Li_4MgSn_2O_7$: Synthesis, phase evolution and microwave dielectric properties

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ABSTRACT

A pure-phase $Li_4MgSn_2O_7$ (L_4MS) was successfully synthesized through optimizing the calcination condition. Microwave dielectric properties of the L_4MS ceramic with the phase evolution were investigated together with its low-temperature sintering. The sample maintains a single L_4MS phase as sintered below 1200 °C, such that τ_f remains a constant value of ~12.4 ppm/°C. Accompanied by the appearance of impurity phases $(Li_2SnO_3)_{ss}$ and especially $(MgO)_{ss}$ at higher sintering temperatures, excellent microwave dielectric properties of $\varepsilon_r = 13.1–13.5$, $Q \times f = 106{,}800–126{,}810$ GHz and $\tau_f = 0–-4.2$ ppm/°C are obtained in samples sintered at 1215–1260 °C for 4 h. Reduction of sintering temperature using LiF sintering aid also helps achieve pure-phase dense L_4MS ceramic. The $L_4MS + x$ wt.% LiF ceramic exhibits $\varepsilon_r \sim 13.7$, Qxf ~ 97,000 GHz ($x \le 3$) and τ_f ~8–13 ppm/°C sintered at 850 °C for potential LTCC applications, and ε_r ~13.9, Qxf ~ 146,000 GHz and τ_f ~1.5–6 ppm/°C ($x \ge 4$) as sintered 1000 °C, exhibiting large potentials for microwave dielectric candidates.

1. Introduction

The Li-based rock-salt structured materials have gained considerable attention in recent years for their large potentials in microwave devices. Li_2TiO_3 gained relatively early attention as possible microwave dielectric candidate materials, followed by its counterparts such as Li_2SnO_3 and Li_2ZrO_3 [1–3]. Although these Li_2BO_3 ceramics are expected to have desirable electrical properties, yet poor microstructure and even microcracks have seriously impeded their potential applications in microwave devices owing to both the easy cleavage on (001) plane and the lithium evaporation at higher sintering temperatures [1–4]. Different ways have been attempted to solve the above issues such as Li-rich atmosphere protection [5,6], liquid-phase sintering [3,7,8] or forming solid solutions with other materials such as MgO, ZnO or NiO [4,9–13], generating significantly improved microwave dielectric properties. In addition, a couple of microwave dielectric materials in Li_2BO_3-AO (B: Sn, Ti, Zr; A: Mg, Zn, Ni) systems have been reported in recent years to exhibit excellent microwave dielectric properties [9,13,14], including Li_2BO_3 solid solutions ($(Li_2BO_3)_{ss}$, AO-structured solid solutions ($(AO)_{ss}$) and/or some compounds [6,7,13–21]. These solid solution ceramics either exhibit a positive temperature coefficient of resonant frequency (τ_f) at the Li_2BO_3-rich side or a negative τ_f at the AO-rich side except for their low-loss features. Among them, $Li_2Mg_3BO_6$ (B: Ti, Sn, Zr) ceramics belonging to the $(MgO)_{ss}$ possess excellent microwave dielectric properties of $\varepsilon_r = 15.2$, 8.8 and 12.6, Qxf = 152,000 GHz (at 8.3 GHz), 123,000 GHz (at 10.7 GHz) and 86,000 GHz (at 9.3 GHz), and $\tau_f = -39$ ppm/°C, −32 ppm/°C and −36 ppm/°C, respectively, at their optimal sintering temperatures [14,16,22]. A higher Qxf value of ~230,000 ~ 330,000 GHz was reported in well-densified $Li_2Mg_3SnO_6$ ceramics by means of sintering aids [7].

As early as 1984, the phase diagram of the $Li_{2/3(1\text{-}x)}Sn_{1/3(1\text{-}x)}Mg_xO$ system was proposed by M. Castellanos and A. R. West [23], in which a β-$(Li_2SnO_3)_{ss}$ single-phase zone, a two-phase zone of β-$(Li_2SnO_3)_{ss}$, $Li_4MgSn_2O_7$ (L_4MS) compound, a wide $(MgO)_{ss}$ single-phase zone, and an additional two-phase zone of $(MgO)_{ss}$ and L_4MS. Recently, the phase structure was further investigated in this system within a wide composition range of x = 0–4/7 except for microwave dielectric properties of some special compositions as reported previously [13]. Of special note is that as new potential dielectric material, microwave dielectric properties of the L_4MS compound has never been reported, although it appears for the first time in the phase diagram of $LiSnO_3$-MgO, and also but only exists later as an impurity phase in some previous studies [7,13,23,24]. The possible reasons might be ascribed to difficulties in pure-phase synthesis and densification behaviors like other Li-based systems [20–26]. In this work, the synthesis processing and sintering of L_4MS ceramics were investigated by means of a conventional solid-state method. Relationship between the phase structure, microstructure and

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microwave dielectric properties was discussed in detail, together with a low-temperature firing of L_4MS ceramics at a temperature of 850 °C.

2. Experimental procedures

The L_4MS ceramics were synthesized by a traditional solid-state reaction method. High-purity powders of MgO, SnO_2 and Li_2CO_3 were used as starting materials. Stoichiometric amounts of the powders were weighed and ball-milled for 10 h using zirconia balls and alcohol as the medium on a planetary milling machine. The resulting slurries were then rapidly dried and calcined at 850–1050 °C for 8–16 h in air. The calcined powders were re-milled for 10 h and then mixed together with 5 wt% PVA as a binder. The granulated powders were subsequently pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. The specimens were first heated at 550 °C in air for 4 h to remove the organic binder, and then sintered at 1120 °C–1275 °C for 4 h. Moreover, the x wt.% LiF sintering aid was added into the as-synthesized pure-phase L_4MS powder and then experienced a sufficient mixing process in alcohol. The L_4MS + x wt.% LiF samples were sintered in air at 800–1075 °C for 4 h. The heating rate was 5 °C/min, and the cooling rate was 10 °C/min. The compacts were muffled with powders of the same composition in an upturned alumina crucible to suppress the lithium evaporation.

The crystal structure of the fired ceramics was identified via an X-ray diffractometer (XRD, D/Max2500 V, Rigaku, Japan) using Cu *Kα* radiation. Rietveld refinements on full profiles of XRD patterns were performed by using the program GSAS to identify the structural parameters of each phase. The bulk densities of the sintered ceramics were measured by the Archimedes method. The microstructure of the pellets was observed using a field-emission scanning electron microscope (FE-SEM; SU8020, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). For the observation of grain morphology, the samples were polished and then thermally etched at a temperature 150 °C lower than the respective sintering temperature for 30 min. Microwave dielectric properties of the ceramic cylinders were measured using a network analyzer (N5230C, Agilent, Palo Alto, CA) and a temperature chamber (GDW-100, Saiweisi, Changzhou, China). The τ_f values of the samples were measured in the temperature range from 20 °C to 80 °C and calculated by the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

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

3. Results and discussion

Fig. 1 shows the XRD patterns of the stoichiometric L_4MS powders calcined under different conditions. Compared with the standard patterns of JCPDS # 31–0761 and JCPDS # 37–1164, it can be seen that Li_2SnO_3 is a dominant phase apart from a slight amount of L_4MS phase as it was calcined at 850 °C for 8 h. With increasing the calcination temperature, L_4MS obviously increases in its phase content, and becomes a main phase in addition to some residual Li_2SnO_3 as the calcination condition is 1050 °C for 8 h, indicating L_4MS has a higher phase formation temperature than Li_2SnO_3. The above results also demonstrate that Li_2O preferentially reacts with SnO_2 at a lower temperature. The reaction kinetic of the resulting Li_2SnO_3 with MgO is so sluggish that both higher calcination temperature and long calcination time are required. A slight amount of residual Li_2SnO_3 phase can be completely eliminated through the calcination at 1000 °C for 16 h, as shown in Fig. 1. Therefore, appropriate calcination temperature and time are two necessary conditions for the synthesis of pure L_4MS phase.

Fig. 2 illustrates normalized XRD patterns of L_4MS ceramics sintered at 1180 °C–1275 °C for 4 h using the pure-phase L_4MS powder. When sintering temperature is lower than 1200 °C, all diffraction peaks can be well indexed according to the L_4MS phase (JCPDS No. 37–1164) and no any other phase can be observed (Fig. 2(a)). An obvious secondary phase of $(Li_2SnO_3)_{ss}$ (JCPDS No. 31–0761) starts to appear as sintering temperature is higher than 1200 °C (Fig. 2(b–g)) and becomes more with further increasing sintering temperature. At the same time, another impurity phase of $(MgO)_{ss}$ (JCPDS No. 39–0932) can be also observed. As sintering temperature is higher than 1230 °C, the L_4MS phase nearly disappears and residual phases are $(MgO)_{ss}$ and $(Li_2SnO_3)_{ss}$ with varying phase content ratio with changing temperature. The phase content and the structure parameter of each phase can be obtained by means of Rietveld refinement of XRD patterns in Fig. 2. Only using samples in Fig. 2(d–g) owing to the lack of information about the unit cell and crystal structure of L_4MS phase, the Rietveld refinement patterns (only for the sample sintered at 1260 °C as an

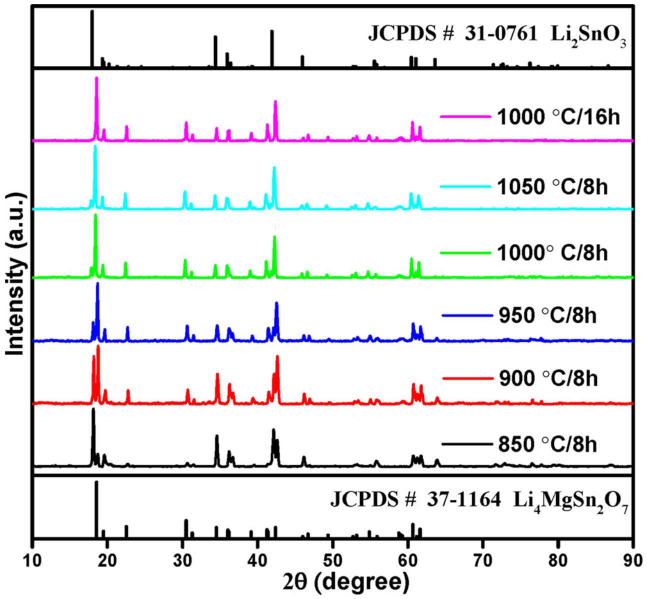

Fig. 1. XRD patterns of L_4MS specimens calcined under various conditions as indicated.

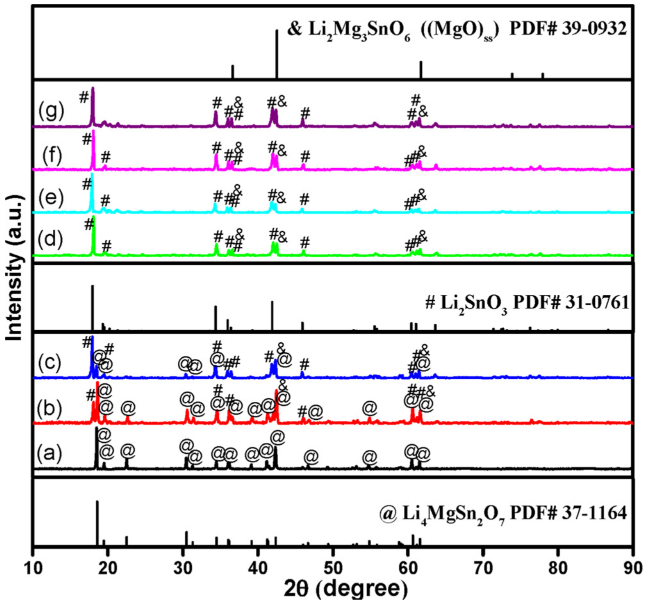

Fig. 2. XRD patterns of L_4MS ceramics sintered at various temperatures for 4 h: (a) 1180 °C, (b) 1200 °C, (c) 1215 °C, (d) 1230 °C, (e) 1245 °C, (f) 1260 °C and (g) 1275 °C.