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Low temperature sintering and microwave dielectric properties of Li_2MgTiO_4-based temperature stable ceramics

Cuijin Pei [a,b], Guoguang Yao [a,*], Peng Liu [c], Jianping Zhou [c]

[a] *School of Science, Xi'an University of Posts and Telecommunications, Xi'an, 710121 China*
[b] *School of Material Science and Engineering, Shaanxi Normal University, Xi'an, 710062 China*
[c] *College of Physics and Information Technology, Shaanxi Normal University, Xi'an, 710062 China*

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ABSTRACT

New temperature-stable Li_2MgTiO_4-10 wt%LiF-12 wt%$Ca_{0.8}Sr_{0.2}TiO_3$(LMT-LiF-CST) composite ceramics with low firing temperature were fabricated via the solid-state reaction method. XRD and SEM-EDS analysis confirmed that $Li_2MgTiO_4$and $Ca_{0.8}Sr_{0.2}TiO_3$ crystal phases can be well coexisted and no secondary phase is included. As for the addition of $Ca_{0.8}Sr_{0.2}TiO_3$, the ε_r and τ_f showed to increase, while $Q \times f$ declined, due to complementation properties of the end members in LMT-LiF-CST. In summary, the LMT-LiF-CST composite ceramics sintered at 900 °C for 5 h showed desirable microwave dielectric properties: $\varepsilon_r=18.0$, $Q \times f=34{,}800$ GHz(at ~8.2 GHz),$\tau_f=4$ ppm/°C, and good chemical compatibility with silver electrode.

1. Introduction

In recent years, with the rapid development of commercial wireless technologies and satellite communication, the low temperature co-fired ceramics (LTCC) technology has played an important role due to its simplicity and advantage in low-cost and miniaturization of multilayer microwave devices [1,2]. Dielectric materials used in LTCC technology must satisfy the following requirements such as high performance (moderate dielectric constant (ε_r), high quality factor ($Q \times f$), near-zero temperature coefficient of resonant frequency (τ_f), low sintering temperature, and chemical compatibility with inner Ag electrode) [3].

Lithium-containing Li_2MgTiO_4 ceramics attracted considerable attention due to its low cost of the production, light weight, and superior microwave dielectric properties ($Q \times f=97{,}300$ GHz, $\varepsilon_r=17.3$ and $\tau_f=-28$ ppm/°C) [4,5]. However, the high sintering temperature and large negative τ_f value preclude its further applications in LTCC technology. Therefore, one purpose in our minds is to lower the sintering temperature of Li_2MgTiO_4 ceramic without much degrading its dielectric properties, the other objective is to compensate for its τ_f. In the present research, Li_2MgTiO_4 ceramics were employed by liquid-phase sintering with LiF additive to decrease their sintering temperature, and $Ca_{0.8}Sr_{0.2}TiO_3$ (τ_f~990 ppm/°C) was used as a τ_f compensator for Li_2MgTiO_4-based ceramics [6]. The effects of LiF and $Ca_{0.8}Sr_{0.2}TiO_3$ addition on the phase compositions, microstructures, chemical compatibility with silver electrode, and microwave dielectric properties of Li_2MgTiO_4-based ceramics were also investigated.

2. Experimental procedure

The starting materials are high-purity oxides or carbonates powders (> 99.9%; Guo-Yao Co. Ltd., Shanghai, China): MgO, TiO_2, Li_2CO_3, $CaCO_3$, and $SrCO_3$. Predried raw materials in stoichiometric Li_2MgTiO_4 and $Ca_{0.8}Sr_{0.2}TiO_3$ compositions were separately weighed and ball-milled for 8 h in a nylon jar with agate balls and ethanol as media. The Li_2MgTiO_4 and $Ca_{0.8}Sr_{0.2}TiO_3$ powders were calcined at 1000 °C for 5 h and 1100 °C for 4 h, respectively. Then, two formulations were prepared and then re-milled for 8 h:

(i) Li_2MgTiO_4-10 wt%LiF (LMT-LiF), (ii)Li_2MgTiO_4-10 wt%LiF-12.0 wt%$Ca_{0.8}Sr_{0.2}TiO_3$ (LMT-LiF-CST). After drying, the powders with 5 wt% polyvinyl alcohol (PVA) as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness under a pressure of 100 MPa. These pellets were sintered from 850 to 925 °C for 5 h in air with a heating rate of 5 °C/min, and then cooled to room temperature. Moreover, in order to evaluate the chemical compatibility with Ag, the LMT-LiF-CST composite powders mixed with 20 wt% Ag powder were ground in an agate mortar, pressed into disks and then sintered at 900 °C for 5 h.

The bulk densities of the sintered ceramics were measured by Archimedes' method. The crystal structures were analyzed using

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* Corresponding author.
E-mail address: yaoguoguang@xupt.edu.cn (G. Yao).

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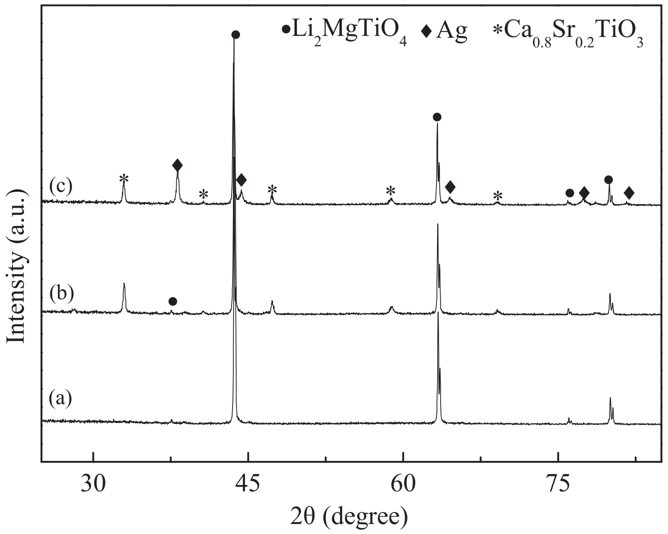


Fig. 1. XRPD patterns of LMT-based ceramics sintered at their individually optimum temperature: (a) LMT-LiF at 875 °C, (b) LMT-LiF-CST at 900 °C, and (c) LMT-LiF-CST-20 wt%Ag at 900 °C.

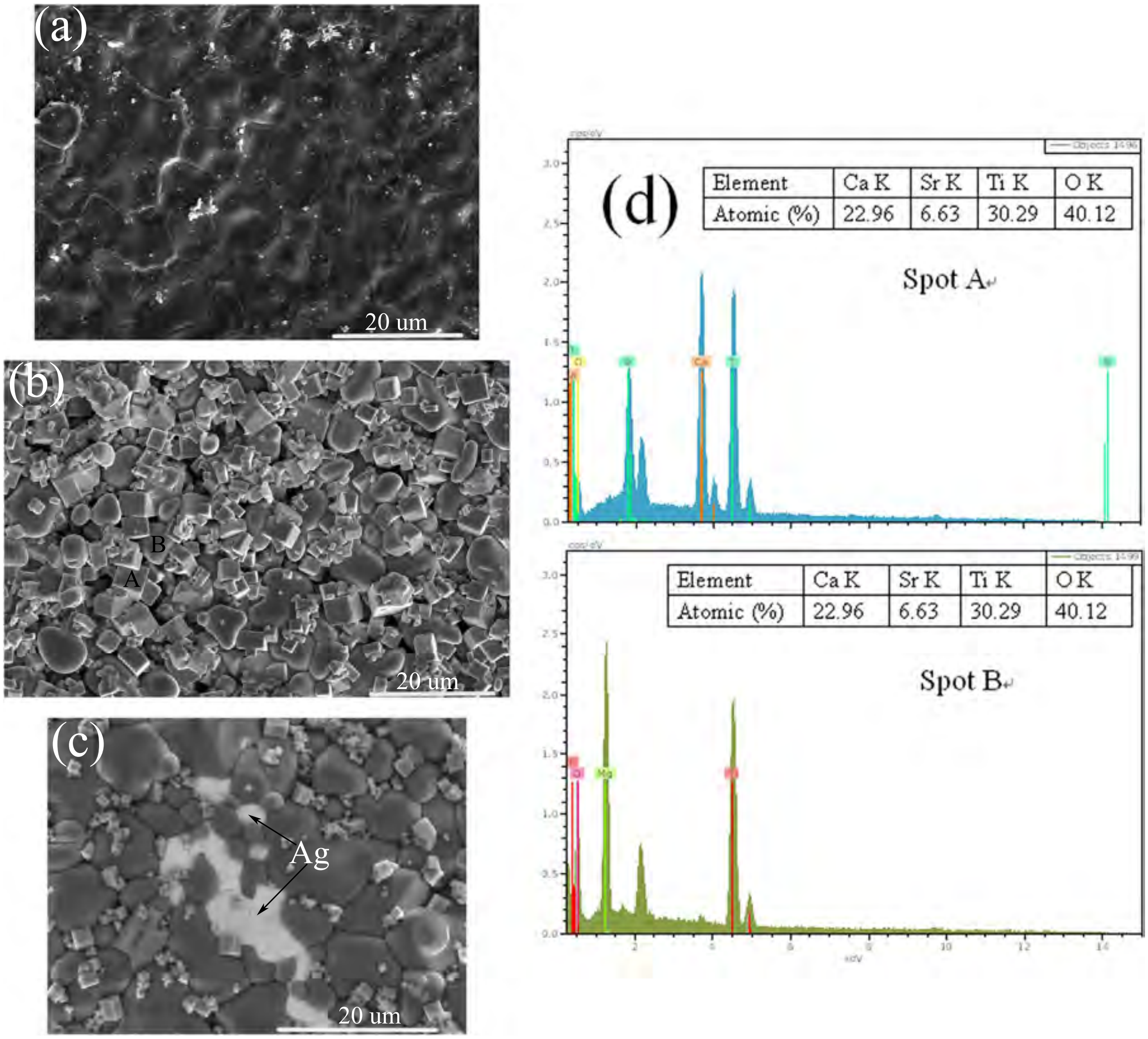
X-ray powder diffraction (XRPD) with Cu Kα radiation (Rigaku D/MAX2550, Tokyo, Japan). The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Eindhoven, Holland) coupled with energy dispersive X-ray spectroscopy (EDS). The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & schwarz, Munich, Germany) with the $TE_{01\delta}$ shielded cavity method. The τ_f was calculated with the following Eq. (1):

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)} \tag{1}$$

where f_{80} and f_{20} are the resonant frequency at 80 °C and 20 °C, respectively.

3. Results and discussions

Fig. 1 shows the XRPD patterns of LMT-based ceramics sintered at their respectively optimum temperature. Pure phase Li_2MgTiO_4 (JCPDS # 89-7118) was obtained for LMT-LiF fired at 875 °C for 5 h, which exhibits a cubic rock salt structure belonging to Fm-3m (225) space group. For LMT-LiF-CST sample, all the peaks can be well indexed by Li_2MgTiO_4 and $Ca_{0.8}Sr_{0.2}TiO_3$ phases (JCPDS #25-0902), and no secondary phase is formed, indicating that a stable two-phase system LMT-LiF-CST can be obtained. Only diffraction peaks of the Ag (JCPDS #89-3722), Li_2MgTiO_4 and $Ca_{0.8}Sr_{0.2}TiO_3$



Element	Ca K	Sr K	Ti K	O K
Atomic (%)	22.96	6.63	30.29	40.12

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Atomic (%)	22.96	6.63	30.29	40.12

Fig. 2. SEM micrographs and EDS spectra of the as-sintered LMT-based ceramics fired at different temperatures: (a) LMT-LiF at 875 °C, (b) LMT-LiF-CST at 900 °C, (c) LMT-LiF-CST-20 wt%Ag at 900 °C, and (d) EDS spectra corresponding to Fig. 2(b).

phases were observed in Fig. 1(c), which indicated that the LMT-LiF-CST composite ceramics exhibits good chemical compatibility with silver electrode at the sintering temperature.

SEM micrographs and EDS spectra of the as-sintered LMT-based ceramics fired at their individually optimal temperature are illustrated in Fig. 2. As shown in Fig. 2(a), the Li_2MgTiO_4 samples by liquid phase sintering with LiF-aids exhibited a dense microstructure with average grain size about 8.7 μm, compared to the SEM micrograph of pure Li_2MgTiO_4 at 1360 °C [5], which having an average grain size less than 4.3 μm as well as some pores existing in the grains. This result indicated that with 10 wt% LiF addition, the densification sintering temperature of Li_2MgTiO_4 ceramic can be effectively lowered from 1360 to 875 °C. Two kinds of grain shapes were seen in Fig. 2(b). By the EDS analysis (Fig. 2(d)) and XRPD result (Fig. 1(b)), the cubic-shape grains (Spot A) are identified as $Ca_{0.8}Sr_{0.2}TiO_3$ phase, while the pebbled-shape grains (Spot B) are defined as Li_2MgTiO_4 phase due to the light element Li could not be detected. No reaction and clear interface between the composite ceramics and Ag were observed in Fig. 2(c), which were in accordance with the results of XRPD result as shown in Fig. 1(c).

The temperature dependence of the ε_r and bulk density in LMT-based ceramics is presented in Fig. 3. The ε_r is dependent on the density, dielectric polarizabilities, molar volume of the compounds, and structural character such as grain boundaries, phase constitution, and compositional homogeneity [7,8]. In this study, the sintering temperature dependence of ε_r values of both ceramics showed a similar tendency with that of bulk density of both ceramics, indicating that the ε_r values are dominated by the bulk density, since a higher density means a lower porosity ($\varepsilon_r=1$) and a higher ε_r. In addition, both the ε_r and density of ceramics decreased with increasing sintering temperature, probably due to the volatilization of Li. Similar phenomena were also developed in other lithium-containing ceramic systems [9–11].

Fig. 4 presents the Q × f and τ_f values of LMT-based ceramics as a function of sintering temperature. In contrast to the ε_r and density, the Q × f values increased with increasing sintering temperature, reaching their individual maximum values of 55,400 GHz for LMT-LiF at 875 °C and 33,700 GHz for LMT-LiF-CST at 900 °C, and then decreased with further increasing temperature, as illustrated in Fig. 4(a). The initial enhancement in Q × f values with increased sintering temperature seemed to be due to the uniform grain size rather than density. The variation in τ_f values of two ceramics with respect to sintering temperature was not significant and remained stable at about −40 ppm/°C and 4 ppm/°C, respectively. Moreover, as expected, with 12 wt% $Ca_{0.8}Sr_{0.2}TiO_3$ addition, the Q × f values of LMT-LiF-CST composite ceramics decreased, whereas its ε_r and τ_f improved, and a near zero τ_f (4 ppm/°C) value could be obtained, which results from complementation properties of the end members in LMT-LiF-CST [5,6].

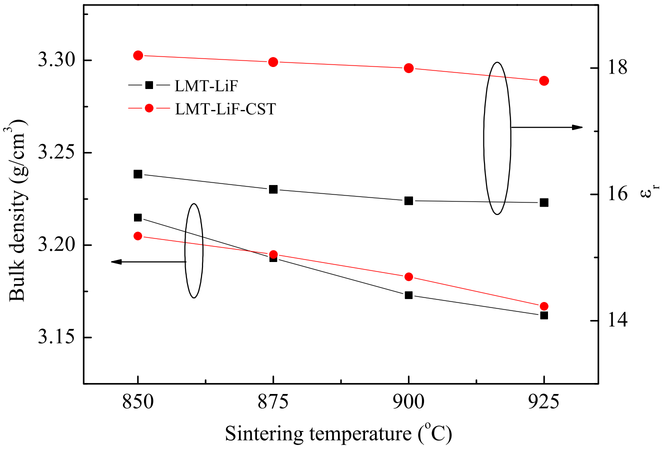

Fig. 3. Bulk density and ε_r of LMT-based ceramics sintered at different temperatures.

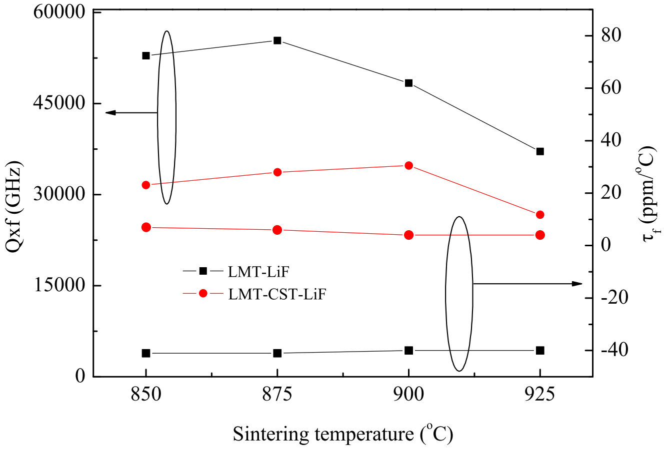

Fig. 4. Variation of Q × f and τ_f values of the LMT-based ceramics as a function of sintering temperature.

4. Conclusion

Low-temperature sinterable LMT-LiF-CST diphasic ceramics were successfully manufactured by a conventional solid-state reaction route. LMT and CST phases coexisted and no secondary phase was found in the sintered ceramics. Typically, the LMT-LiF-CST composite ceramic sintered at 900 °C processed chemical compatibility with silver electrode and desirable microwave dielectric properties of $\varepsilon_r=18.0$, Q × f=34 800 GHz (at ~8.2 GHz), and $\tau_f=4$ ppm/°C. These merits make it an alternative candidate material for LTCC applications.

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