Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 38 (2012) 2239–2242
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of LiF addition on sintering behavior and microwave dielectric properties of $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ ceramics

G.G. Yao [a,b,*], P. Liu [a]

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

Received 28 July 2011; received in revised form 24 October 2011; accepted 31 October 2011
Available online 4 November 2011

Abstract

The effects of LiF addition on the sinterability and microwave dielectric properties of $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) ceramics were investigated. A small amount of LiF addition can effectively lower the sintering temperature of MZTS from 1325 °C to 1150 °C due to the liquid phase effect and induce no apparent degradation of the microwave dielectric properties. With increasing LiF content, the apparent density and dielectric constant decreased gradually, the quality factor increased firstly and then decreased. In particular, MZTS–3.0 wt% LiF ceramics sintered at 1150 °C for 5 h exhibited good microwave dielectric properties of $\varepsilon_r = 13.05$, $Q \cdot f = 119{,}310$ GHz (at 10 GHz) and $\tau_f = -59.2$ ppm/°C.

Keywords: C. Dielectric properties; D. Spinels; Liquid phase sintering

1. Introduction

Ever since the carrier frequency of interest in communication systems is extended from microwave to millimeter wave range, much attention has been paid to the dielectric properties of materials at microwave and millimeter wave frequency for wireless communication systems [1]. Dielectric ceramics applicable to millimeter wave frequency should have a high quality factor ($Q \cdot f$, where Q = 1/dielectric loss and f is the resonant frequency) for frequency selectivity, and a relatively low dielectric constant (ε_r), in order to minimize the cross-coupling effect with the conductor and increase the signal propagation velocity. Besides, the basic physical property requirement, the cost, and the toxicity should also be considered in these applications [2,3]. However, most of the currently available low-loss dielectrics are made from complex perovskites [4–6]. They require high sintering temperatures and compatibly high cost. Therefore, the research for new low-cost dielectric ceramics with a high $Q \cdot f$ and low ε_r is still ongoing.

Mg_2TiO_4 ceramic is a high $Q \cdot f$ and low-cost material for high frequency applications. It has a spinel structure belonging to the cubic space group $Fd\bar{3}m$ [7,8]. Belous et al. first reported its microwave dielectric properties ($\varepsilon_r = 14$, $Q \cdot f = 150{,}000$ GHz, and $\tau_f = -50$ ppm/°C) [9]. Presently active works have been done to improve its microwave dielectric properties by suitable ions substitution, preparing various composites [10–15]. Among these, Huang et al. reported an improvement in $Q \cdot f$ of Mg_2TiO_4 series by partial substitution for Mg or Ti-site ions, and we reported the Zn–Sn codoped $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) ceramics sintered at 1325 °C, which possesses good microwave dielectric properties ($\varepsilon_r = 13.1$, $Q \cdot f = 131{,}170$ GHz, and $\tau_f = -55.6$ ppm/°C) [16]. However, its sintering temperature is still too high for practical use. It is well known that LiF is an effective sintering aid for many materials [17,18]. For example, the $MgTiO_3$ dielectric ceramic can be sintered at 950 °C by the addition of LiF. In the present work, the effluence of LiF addition on the sintering behavior, phase constituents and microwave dielectric properties of MZTS ceramics were studied.

2. Experimental

The starting materials are high-purity oxide powders (>99.9%): TiO_2, MgO, ZnO and SnO_2. Predried raw materials were weighed in stoichiometric $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$

* Corresponding author at: School of Science, Xi'an University of Posts and Telecommunications, Xi'an 710121, China. Tel.: +86 29 88166089.
E-mail address: yaoguoguang@xupt.edu.cn (G.G. Yao).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.073

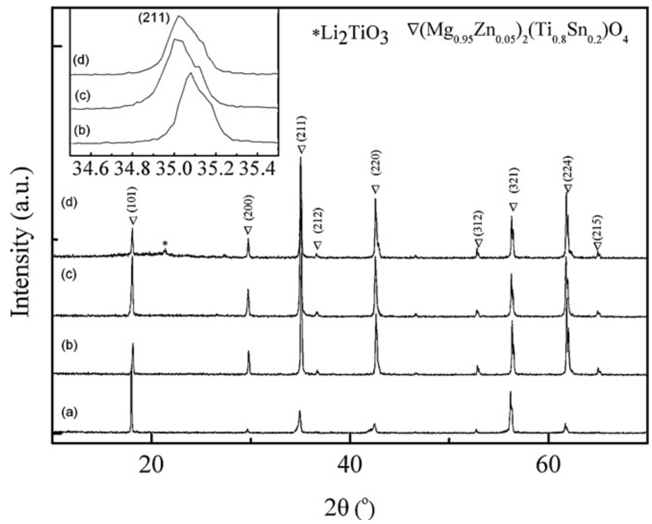

Fig. 1. X-ray diffraction of $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$–$x$ wt% LiF (MZTS–x wt% LiF) ceramics: x = 0, 1325 °C and (b) x = 1.5, (c) x = 3.0, and (d) x = 4.5 sintered at 1150 °C.

(MZTS) and ball milled for 6 h in a nylon jar with agate balls and ethanol as media. The milled powders were dried then initially calcined at 1150 °C for 3 h. The as-calcined powders were re-milled with various LiF additions for 6 h. After drying, the powders with 5 wt% PVA as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness under a pressure of 200 MPa. The green compacts were sintered between 1100 °C and 1175 °C for 5 h in air.

The apparent densities of the sintered ceramics were measured by Archimedes' method. The crystal structures were analyzed using X-ray diffraction (XRD) with Cu Ka radiation (Rigaku D/MAX2550, Japan). The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Holland). The reactions of the calcined powders with LiF addition taking place during sintering process were investigated by differential thermal analysis (DTA-TGA, SDTQ600, USA) using a heating rate of 10 °C/min in air from room temperature up to 1200 °C. The microwave dielectric properties of sintered samples at microwave frequency were measured using a network analysis (HP8720ES, Agilent, Palo Alto, CA) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns of MZTS–x wt% LiF specimens sintered at different temperatures. Pure MZTS sample sintered at 1325 °C exhibits a cubic spinel structure with space group $Fd\bar{3}m$, with no second phase detected. When $x \leq 3.0$, a single phase MZTS, without second phase, was detected within the detectable level of XRD. Moreover, minor amount of second phase Li_2TiO_3 was

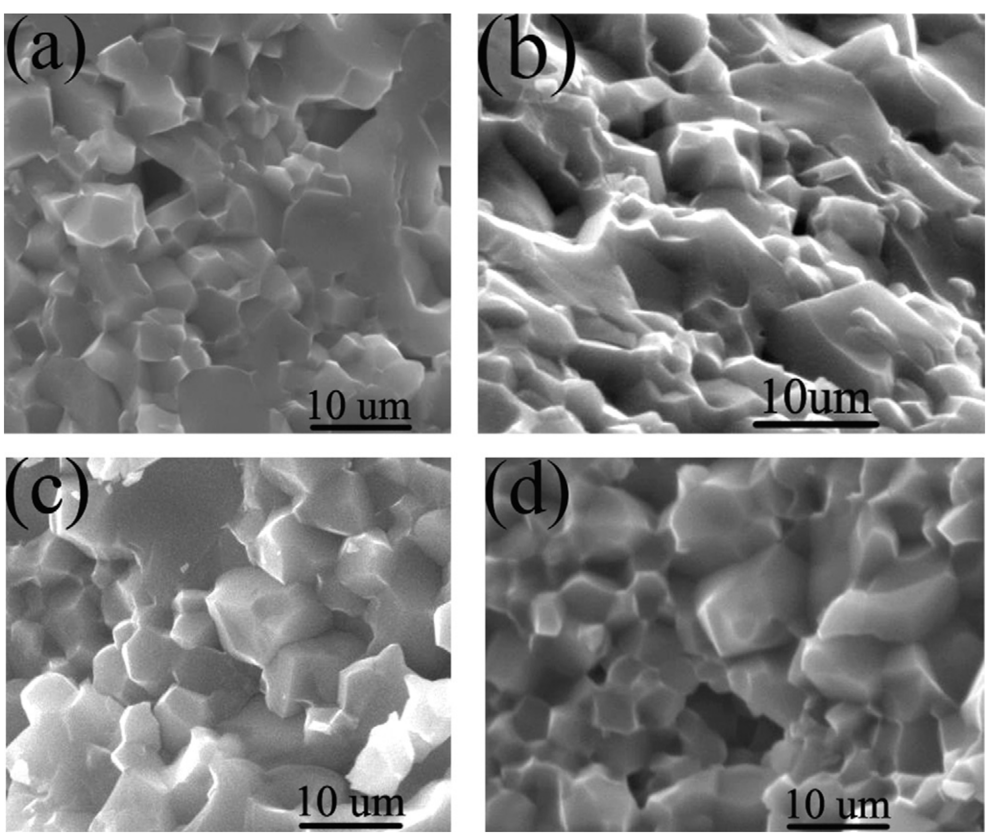

Fig. 2. Typical SEM images of the fractured surfaces of MZTS–x wt% LiF ceramics sintered at different temperatures: (a) 1.5 = 0, 1125 °C (b) x = 3.0, 1125 °C, (c) 4.5, 1125 °C, (d) x = 3.0, 1150 °C, and (e) x = 3.0, 1175 °C.

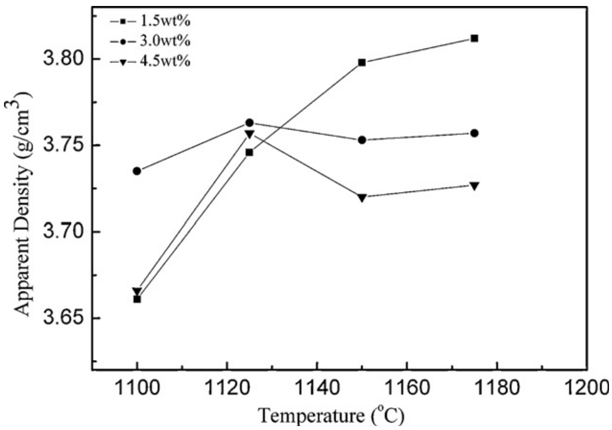

Fig. 3. Apparent densities of MZTS–x wt% LiF ceramics as a function of sintering temperature.

developed for $x = 4.5$. It was considered that some of Ti ions in the matrix dissolved into the liquid phase and that the Li_2TiO_3 second phase was formed. Furthermore, as shown in the insert of Fig. 1, the main peak (2 1 1) of MZTS–x wt% LiF shifted slightly toward to lower angle with increasing LiF content. This indicated that a small amount of Li^+ was incorporated into the matrix of specimen. Similar result was reported in the case of LiF doped $MgTiO_3$ ceramics by Bernard et al. [18].

Typical SEM micrographs of the fractured surfaces of MZTS–x wt% LiF ceramics sintered at different temperatures are illustrated in Fig. 2. For the samples sintered at 1125 °C, the number of pores decreased with increasing x, as shown in Fig. 2(a)–(c). For the specimens containing 3.0 wt% LiF, the abnormal grain growth and porous microstructure were observed with increasing sintering temperature, which could damage its microwave dielectric properties. Moreover, the grain morphology of MZTS–x wt% LiF ceramics is also characteristic of liquid sintering.

Fig. 3 exhibits the apparent density of MZTS–x wt% LiF samples as a function of sintering temperature. In the case of $x = 1.5$, the density of the samples increased as the sintering temperature increased. For the specimens with $x \geq 3.0$, with the increasing temperature, the density increased firstly then decreased thereafter. Moreover, in the temperature range from 1100 °C to 1150 °C, at the same fired temperature, the density of the specimens increased firstly and then decreased as LiF content increased. Densification of MZTS–3.0 wt% LiF is completed at around 1125 °C, which is much lower than that of pure MZTS (1325 °C). This indicates that LiF is an effective sintering aid for MZTS ceramics.

In order to identify the role of LiF on the sintering behavior of MZTS, TG-DTA analyses were performed as shown in Fig. 4. The TG curve shows two distinct weight losses. In the temperature range from room temperature to 500 °C, the DTA curve shows two exothermic peaks, which are related to the first weight loss. Those peaks are considered to be caused by the combustion of the organic binders [19]. Moreover, three distinct endothermic peaks were observed in the temperature range of 700–1100 °C, which are related to the second weight loss. The endothermic peaks at ~784 °C, and 1025 °C are attributed to the eutectic melting point fluxes between LiF–MgF_2 [20,21] and the endothermic peak at ~885 °C corresponds to meting of LiF [22], which enhance the sintering ability of MZTS–x wt% LiF ceramics.

Fig. 5 illustrates the ε_r and $Q \cdot f$ of MZTS–x wt% LiF ceramics sintered at different temperatures. The trend of ε_r of MZTS–x wt% LiF (except $x = 4.5$), as shown in Fig. 5(a), which depended on the sintering temperature, was consistent with that of the density. For the specimens containing 4.5 wt%

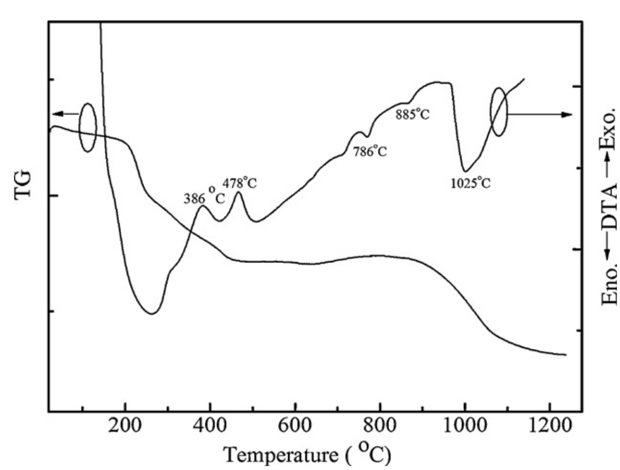

Fig. 4. DTA–TG curves of calcined MZTS powders with 3.0 wt% LiF addition.

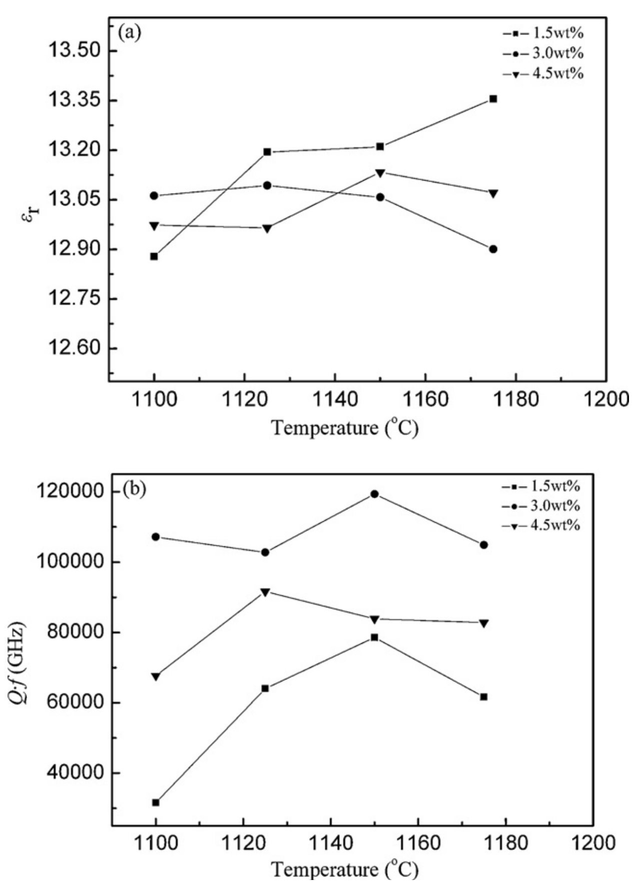

Fig. 5. Variation of (a) ε_r and (b) $Q \cdot f$ values of MZTS–x wt% LiF ceramics sintered at various temperatures.

LiF, the maximum ε_r value was obtained at 1150 °C, although its density was slightly lower than that the sample sintered at 1125 °C. This may be attributed to the second phase Li_2TiO_3 (see Fig. 1(d)), which possesses a higher ε_r ($\varepsilon_r = 19.75$) [23]. From Fig. 5(b), it can be observed that the $Q \cdot f$ values increased with increasing sintering temperature and then decreased after reaching their respective maximum value. The increase in the $Q \cdot f$ value can be solely attributed to an increase in the density, whereas its decrease at higher temperature is due to the abnormal grain growth, as observed in Fig. 2(e). Moreover, when the content of LiF was increased from 3.0 to 4.5 wt%, the $Q \cdot f$ values for specimens sintered at 1150 °C decreased from 119,310 to 84,000 GHz, which could be attributed to the second phase Li_2TiO_3 ($Q \cdot f \sim 23{,}600$ GHz) [23]. In the present case, a maximum $Q \cdot f$ value of 119,310 GHz is obtained for the composition with $x = 0.3$ sintered at 1150 °C.

4. Conclusions

The sintering temperature of $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) ceramics is lowered from 1325 °C to 1150 °C by addition of 3.0 wt% LiF. A second phase Li_2TiO_3 was formed when the LiF exceeded 3.0 wt%, which affects the microwave dielectric properties of MZTS. With increasing LiF content, the apparent density and dielectric constant decreased gradually, the quality factor increased firstly and then decreased. In particular, MZTS–3.0 wt% LiF ceramics sintered at 1150 °C for 5 h exhibited good microwave dielectric properties of $\varepsilon_r = 13.05$, $Q \cdot f = 119{,}310$ GHz (at 10 GHz) and $\tau_f = -59.2$ ppm/°C.

Acknowledgements

This work was supported by the Nature Scicence Foundation of China (Grant nos. 51072110 and 51132003), Open Fund of state Key Laboratory of Electronic Films and Integrated Devices, UESTC (Grant no. KFJJ201106), and Shaanxi Province Department Education (Grant no. 11JK0829).

References

[1] N. Mori, Y. Sugimoto, Y. Higuchi, Dielectric properties of new glass–ceramics for LTCC applied to microwave or millimeter-wave frequencies, J. Eur. Ceram. Soc. 26 (2006) 1925–1928.

[2] T. Joseph, M.T. Sebastian, Microwave dielectric properties of $(Sr_{1-x}A_x)_2(Zn_{1-x}B_x)Si_2O_7$ ceramics (A = Ca, Ba and B = Co, Mg, Mn, Ni), J. Am. Ceram. Soc. 93 (2010) 147–154.

[3] D. Zhou, C.A. Randall, H. Wang, X. Yao, Ultra-low firing high-k scheelite structures based on $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ microwave dielectric ceramics, J. Am. Ceram. Soc. 93 (2010) 2147–2150.

[4] H. Tamura, T. Konoike, Y. Sakabe, K. Wakino, Improved high-Q dielectric resonator with complex structure, J. Am. Ceram. Soc. 67 (1984) c59–c61.

[5] H.J. Kim, S. Kucheiko, S.J. Yoon, H.J. Jung, Microwave dielectrics in the $(La_{1/2}Na_{1/2})TiO_3$–$Ca(Fe_{1/2}Nb_{1/2})O_3$ system, J. Am. Ceram. Soc. 80 (1997) 1316–1318.

[6] M.S. Fu, X.Q. Liu, X.M. Chen, Y.W. Zeng, Microstructure and microwave dielectric properties of $(1-x)Ca(Mg_{1/3}Ta_{2/3})O_3$–$x$$CaTiO_3$ ceramics, J. Am. Ceram. Soc. 91 (2008) 1163–1168.

[7] B.A. Wechsler, R.B. Dreele, Structure refinements of Mg_2TiO_4, $MgTiO_3$ and $MgTi_2O_5$ by time-of-flight neutron powder diffraction, Acta Crystallogr. B 45 (1989) 542–549.

[8] M. Isobe, Y. Ueda, Synthesis, structure and physical properties of spinel solid solutions Mg_2TiO_4–$MgTi_2O_4$, J. Alloys Compd. 383 (2004) 85–88.

[9] A. Belous, O. Ovchar, D. Durilin, High-Q microwave dielectric materials based on the spinel Mg_2TiO_4, J. Am. Ceram. Soc. 89 (2006) 3441–3445.

[10] A. Belous, O. Ovchar, D. Durylin, M. Valant, D. Suvorov, Microwave composite dielectrics based on magnesium titanates, J. Eur. Ceram. Soc. 27 (2007) 2963–2966.

[11] C.L. Huang, J.Y. Chen, C.Y. Jiang, Dielectric characteristics and sintering behavior of Mg_2TiO_4–$(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system at microwave frequency, J. Alloys Compd. 487 (2009) 420–424.

[12] C.L. Huang, S.S. Liu, Low-loss microwave dielectrics in the $(Mg_{1-x}Zn_x)_2TiO_4$ ceramics, J. Am. Ceram. Soc. 91 (2008) 3428–3430.

[13] C.L. Huang, J.Y. Chen, High-Q microwave dielectrics in the $(Mg_{1-x}Co_x)_2$-$)_2TiO_4$ ceramics, J. Am. Ceram. Soc. 92 (2009) 379–383.

[14] C.L. Huang, J.Y. Chen, Low-loss microwave dielectrics using $Mg_2(Ti_{1-x}Sn_x)O_4$ ($x = 0.01$–0.09) solid solution, J. Am. Ceram. Soc. 92 (2009) 2237–2241.

[15] H. Zhu, W.Z. Lu, W. Lei, Microwave dielectric properties of the $(1-x)Mg_2TiO_4$–$x$$CaTiO_3$–$y$ wt.% $ZnNb_2O_6$ ceramics system, Ceram. Int. 37 (2011) 1515–1519.

[16] G.G. Yao, P. Liu, Microwave dielectric properties of low-loss $(Mg_{0.95}Zn_{0.05})$2$(Ti_{0.8}$Sn0.2)O$_4$ ceramics, J. Funct. Mater. 42 (2011) 732–733.

[17] J.X. Tong, Q.L. Zhang, H. Yang, J.L. Zou, Low-temperature firing and microwave dielectric properties of $Ca[(Li_{0.33}Nb_{0.67})_{0.9}Ti_{0.1}]O_{3-\delta}$ ceramics with LiF addition, Mater. Lett. 59 (2005) 3252–3255.

[18] J. Bernard, D. Houivet, M. Hervieu, J.M. Haussonne, Evidence of the formation of a new rock-salt type compound Li_2MgTiO_4 and of its role on the properties of the Li doped $MgTiO_3$, Solid State Sci. 8 (2006) 598–605.

[19] T.H. Fang, Y.J. Hsiao, L.W. Ji, S.S. Chi, Structural and luminescent properties of $Mg_4Nb_2O_9$ nanocrystals, J. Cryst. Growth 310 (2008) 3331–3334.

[20] J. Bernard, D. Houivet, J.E. Fallah, J.M. Haussonne, $MgTiO_3$ for Cu base metal multilayer ceramic capacitors, J. Eur. Ceram. Soc. 24 (2004) 1877–1881.

[21] W.E. Counts, E.F. Osborn, Fluoride model systems: 11. The binary systems CaF, –BeF, MgF, –BeF, and LiF–MgF_2, J. Am. Ceram. Soc. 36 (1953) 12–17.

[22] M. Pollet, S. Marinel, Low temperature sintering of $CaZrO_3$ using lithium fluoride addition, J. Eur. Ceram. Soc. 23 (2003) 1925–1933.

[23] L.X. Pang, D. Zhou, Microwave dielectric properties of low-firing Li_2MO_3 (M = Ti, Zr, Sn) ceramics with B_2O_3–CuO addition, J. Am. Ceram. Soc. 93 (2010) 3614–3617.