J Mater Sci: Mater Electron
DOI 10.1007/s10854-017-7013-4

Microwave dielectric ceramic of $LiZnPO_4$ for LTCC applications

C. C. Xia[1] · D. H. Jiang[1] · G. H. Chen[1] · Y. Luo[1] · B. Li[1] · C. L. Yuan[1] · C. R. Zhou[1]

Received: 22 January 2017 / Accepted: 22 April 2017

Abstract The feasibility of $LiZnPO_4$ (LZP) ceramic prepared by a solid-state reaction method for low-temperature co-fired ceramic application was investigated. Dense ceramic with 94.37% relative density was obtained when the ceramic was sintered at 850 °C for 4 h. The LZP ceramic sintered at 850 °C for 4 h possessed a relative permittivity (ε_r) of 5.3 and high quality factor ($Q\times f$) of 28,496 GHz (at 12.9 GHz) with a temperature coefficient of resonant frequency (τ_f) of −80.4 ppm/°C. The relatively large negative τ_f value was reduced by adding TiO_2 into LZP ceramics. The microstructure, microwave dielectric properties and cofiring compatibility with silver of LZP–TiO_2 composites were discussed. The composite with 0.17 volume fraction of TiO_2 sintered at 950 °C for 4 h shows $\varepsilon_r = 10.0$, $Q\times f = 10{,}025$ GHz, $\tau_f = +1.6$ ppm/°C. The LZP-TiO_2 composite was chemically compatible with the commonly used electrode material silver.

1 Introduction

With the rapid development of microwave telecommunication industry, various microwave dielectric materials and devices such as duplexers, resonators, antennas and oscillators, have been widely used and investigated for several decades [1]. Meanwhile, the widespread use of microwave communication accelerated the search for new technologies to produce miniaturized microwave devices. Among the latest technologies, low-temperature co-fired ceramics (LTCC) technology has proven its potential in developing high-density, low-cost modules for high-performance electronic systems and is required for miniaturization and integration of microwave components for wireless communication [2]. The material selection plays a crucial role in determining the final performance of the modules. As we know, microwave dielectric materials should possess low dielectric constant (ε_r), low loss (high quality factor[$Q\times f$], $Q = 1/\tan\delta$, f = microwave frequency) and near zero temperature coefficient of resonant frequency (τ_f) in order to utilize them as microwave dielectric for microwave communication [3, 4]. Furthermore, the microwave dielectric materials for LTCC applications have to be sintered below the melting point (961 °C) to actualize co-firing with conventional cheap silver (Ag) electrode. To reduce the firing temperature of microwave dielectric materials, there are basically two effective methods: (i) the addition of low melting oxides and glasses into the ceramic, and (ii) the use of ultra fine powders synthesized through wet chemical processing. The decrease of $Q\times f$, however, is chief shortcoming for the first method. For the second method, complex process and high cost undoubtedly limit its application. The most competitive method is to use ceramics having inherent low densification temperature. Therefore, there is an ever-growing need for novel additive-free microwave ceramics with good dielectric properties and low firing temperature.

Recently, some lithium-transition metal phosphates $LiMPO_4$ (M = Fe, Mn, Co, Ni) with olivine structure were reported to be attractive for LTCC applications because these compounds have relatively low melting point and can be sintered below 900 °C [5]. However, most investigation is focused on the electrochemical and illuminant properties of the $LiMPO_4$ [6, 7]. More recently, Hu et al. [8] studied dielectric relaxation and microwave dielectric

✉ G. H. Chen
cgh1682002@163.com; chengh@guet.edu.cn

[1] School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

Published online: 28 April 2017

properties of low sintered $LiMnPO_4$ ceramics. However, large negative value (90–101 ppm/°C) restricts its practical application. And the compatibility of the $LiMnPO_4$ ceramic with an Ag electrode had not been studied. Thomas et al. [9] reported $LiMgPO_4$ ($\varepsilon_r = 6.6$, $Q \times f = 79{,}100$ GHz, and $\tau_f = -55$ ppm/°C) ceramic can be cofired with silver. To date, there are no reports on the microwave dielectric properties of $LiZnPO_4$ (LZP) for LTCC applications.

In this work, LZP ceramic was prepared via the solid state reaction method for the first time. The firing, microstructure, microwave dielectric properties were systematically studied. Moreover, to further improve the dielectric properties, TiO_2 was selected to tune the temperature coefficient of resonant frequency (τ_f) to near zero and increase the permittivity (ε_r) as well as not deteriorate and $Q \times f$ value. Meanwhile, the influences of TiO_2 additive on the phase purity, microstructure, and microwave dielectric properties of LZP ceramics, and the compatibility of the LZP-TiO_2 composite with an Ag electrode have also been studied. These new LTCC ceramic materials with good microwave dielectric properties can address the growing demand of LTCC technology.

2 Experimental procedures

$LiZnPO_4$ (LZP) ceramic was synthesized by the conventional solid state reaction route. Analytical grade powders of Li_2CO_3, ZnO, $NH_4H_2PO_4$ and TiO_2 were used as the starting materials. The raw oxide materials were weighted according to the stoichiometric ratio and ball milled in ethanol medium for 4 h in nylon jars using yttria stabilized zirconia balls. The mixture was calcined at 600 °C in air for 4 h. The calcined LZP powders were remilled together with different volume percentages of TiO_2 (14–21 vol%) in alcohol medium for 24 h. After drying, and mixing with 5 wt% polyvinyl alcohol (PVA) solution, the granulated powders were pressed uniaxially into pellets of 12 mm in diameter and 6–7 mm in thickness under a pressure of 100 MPa. The pellets were then fired at 600 °C for 1 h to expel the binder before sintering at temperatures in the range of 775–950 °C for 4 h in air.

The bulk density was measured by using the Archimedes method. The phase structure was identified by X-ray diffraction (XRD) technique using CuKa radiation (Bruker D8 Advance, Germany). The surface microstructure of the specimens was evaluated by field scanning electron microscopy (SEM) (Quanta 600 FEG, FEI) coupled with energy-dispersive X-ray spectroscopy (EDS). Dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (N5230C, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25–75 °C. The temperature coefficient of resonant frequency (τ_f) was measured by noting the variation of resonant frequency of the TE_{011} resonant mode over the temperature range. To check the chemical compatibility between the ceramic and the silver powder, 20 wt% silver was mixed with the LZP + TiO_2 powder, and then the pressed pellets were fired at 900 °C for 4 h to achieve equilibrium.

3 Results and discussion

Figure 1 shows the powder XRD patterns of LZP ceramics sintered at various temperatures for 4 h. All the diffraction peaks are indexed JCPDS file number 79-0804 for $LiZnPO_4$, and no additional peaks are observed. The SEM micrographs of the surface for pure LZP ceramic sintered at different temperatures 4 h are depicted in Fig. 2. At 775 °C, the sample presents not too dense microstructure with average grain size of 1 μm shown in Fig. 2a. Raising temperature leads to the porosity decreasing and grain size increasing seen in Fig. 2b–d. At 850 °C, the dense uniform microstructure with average grain size of 5 μm is observed and the grain boundary is clear, as shown in Fig. 2c. With further increasing temperature to 875 °C, obviously asymmetrical microstructure is formed shown in Fig. 2d, which is probably owing to excessive sintering temperature resulting in slightly evaporation of Li during firing process.

Figure 3a shows the bulk and relative densities of LZP ceramic as a function of sintering temperature. The bulk and relative densities display a similar variation trend with the increment of temperature. The theoretical density of the $LiZnPO_4$ ceramic is 3.285 g cm^{-3} [10]. The maximal relative density of 94.37% at 850 °C

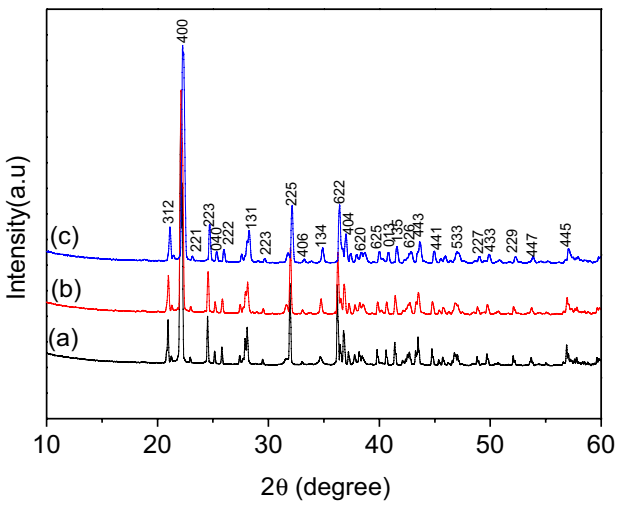

Fig. 1 XRD patterns of LZP ceramics sintered at various temperatures for 4 h: *a* 775 °C, *b* 850 °C, *c* 875 °C

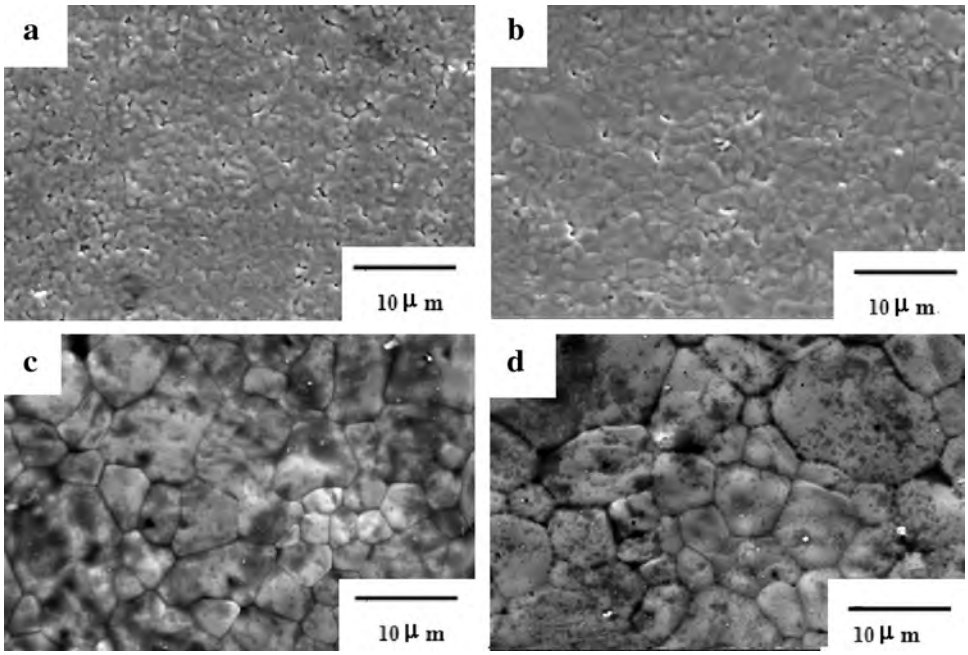

Fig. 2 SEM images of the $LiZnPO_4$ ceramic sintered at various temperatures for 4 h: **a** 775 °C, **b** 800 °C, **c** 850 °C, **d** 875 °C

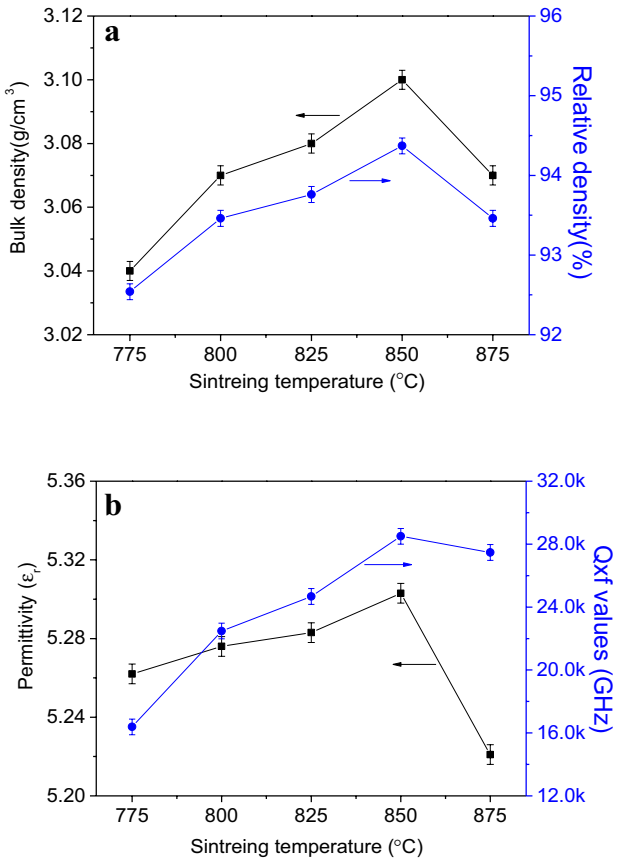

Fig. 3 **a** Variation of bulk density and relative density of LZP ceramics, **b** permittivity (ε_r) and $Q\times f$ values of LZP ceramics as a function of sintering temperature

is reached. The decrease of relative density at 875 °C may be due to over-burning and heterogeneous exaggerated grain growth. The changes in permittivity and $Q\times f$ value of the ceramics with firing temperature are illustrated in Fig. 3b. It is observed that the permittivity firstly increases, reaches a maximum value of 5.3 at 850 °C, and then decreases with increasing temperature. Generally, the permittivity at microwave frequency depends on the relative density and secondary phases, etc [11]. The effect of secondary phase on the permittivity can be neglected since there is no any secondary phase in XRD patterns. The variation in permittivity with sintering temperature is in well agreement with that in relative density. It is clear that the saturation of $Q\times f$ value occurs at 850 °C shown in Fig. 3b. The $Q\times f$ value decreases with further increase of sintering temperature, which may be attributed to the low densification. The as-prepared LZP ceramic sintered at 850 °C possesses a ultimate $Q\times f$ value of 28,496 GHz (at 12.9 GHz) and a relatively large negative value of τ_f (−80.4 ppm/°C). Apparently, its high negative τ_f is not suitable for practical applications. The big negative value of τ_f can be lowered by introducing TiO_2 with a high-positive τ_f (~450 ppm/°C) in the LZP ceramics.

Figure 4 shows the XRD patterns of LZP–TiO_2 composites with various volume percentage of TiO_2 sintered at 950 °C for 4 h. It is found that the mixture of $LiZnPO_4$ (PDF#79-0804) and TiO_2 (PDF#21-1276) coexists for all the compositions, and no other phases are observed. This means that no chemical reaction between LZP and TiO_2 occurs. The big difference in crystal structure and good stability of both phases restrain the chemical reaction between LZP and TiO_2 [12].

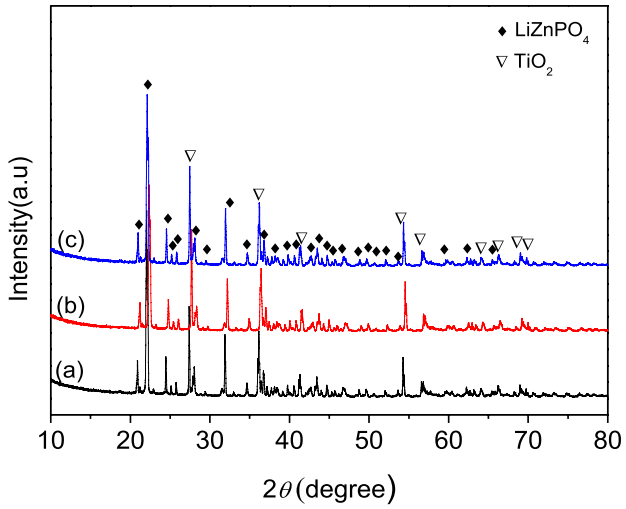

Fig. 4 XRD patterns of LZP–TiO_2 composites with different volume fraction of TiO_2 sintered at 950 °C 4 h: *a* 0.15, *b* 0.17, *c* 0.19

Figure 5 shows the SEM micrographs of LZP–TiO_2 composites with different volume percentage of TiO_2 sintered at 950 °C for 4 h. All the samples containing TiO_2 exhibit a pronounced difference in microstructure compared with the specimen without TiO_2 shown in Fig. 2c, namely, both of large grains and fine grains coexist, as shown in Fig. 5. As a whole, all the samples present a dense microstructure. However, adding 0.19 volume fraction of TiO_2 has somewhat adverse effect on the densification. It is well known that the melting point of TiO_2 is very high (>1800 °C) [13]. Hence, the diffusion rate of ions is very low at low sintering temperature. It is guessed that the grain refining may be owing to the function of TiO_2. In other words, the addition of TiO_2 increase the sintering temperature and change the grain morphology and grain size.

The microwave dielectric properties of LZP–TiO_2 composites sintered at 950 °C for 4 h are listed in Table 1. With the increment of TiO_2, the permittivity of the composites increases, which is due to that TiO_2 has a large value of ε_r (~100) [13]. A reduction in $Q\times f$ with the increase in TiO_2 volume fraction may be mainly due to the following reasons: (i) the decrease in the densification. (ii) possible electrical inhomogenity produced by the mixing of two materials with largely different ε_r values.(iii) nonuniform mixing of phases causing detrimental effects on $Q\times f$. The τ_f is well known to be governed by the composition. Because the τ_f values of the LZP and TiO_2 are about negative 80 ppm/°C and positive 411 ppm/°C, respectively, the increment of TiO_2 content makes the τ_f value become more positive. It implies that zero τ_f can be easily achieved by adjusting the amount of

Table 1 Microwave properties of $LiZnPO_4$–TiO_2 composites with different volume fraction of TiO_2 fired at 950 °C for 4 h

Volume fraction of TiO_2	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
0	5.5	28,496	−80.2
0.14	8.3	13,844	−24.0
0.15	8.8	11,769	−21.5
0.17	10.0	10,025	1.6
0.19	10.7	10,552	7.8
0.21	10.9	10,738	24.3

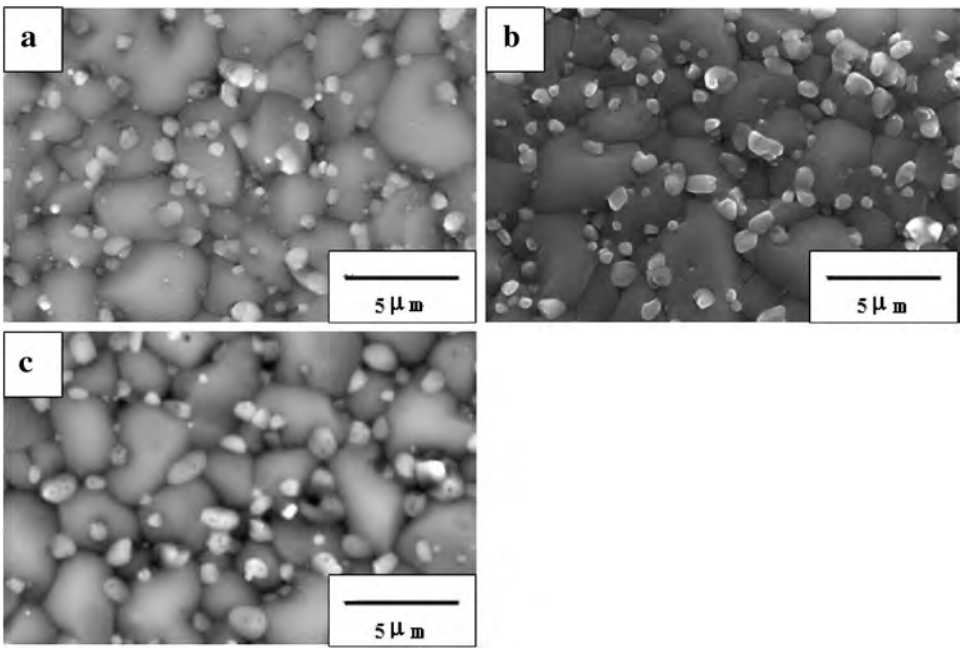

Fig. 5 SEM images of LZP–TiO_2 composites with different volume fraction of TiO_2 sintered at 950 °C for 4h: **a** 0.15, **b** 0.17, **c** 0.19

TiO_2 content. Typically, the LZP with 0.17 volume fraction of TiO_2 has good microwave dielectric properties of $\varepsilon_r = 10.0$, $Q \times f = 10{,}025$ GHz, $\tau_f = 1.6$ ppm/°C, as shown in Table 1. Further investigations are required to improve the $Q \times f$ value for application in wireless communication systems.

The theoretical permittivity (ε_r) of $LiZnPO_4$–TiO_2 composites with different volume fraction of TiO_2 sintered at 950 °C for 4 h can be calculated using different existing models and expression. The mathematical equations of each model are described as follows:

Series mixing model [14]:

$$\frac{1}{\varepsilon_r} = \frac{(1-x)}{\varepsilon_{r_1}} + \frac{x}{\varepsilon_{r_2}} \tag{1}$$

Paralell mixing model [15]:

$$\varepsilon_r = (1-x)\varepsilon_{r_1} + x\varepsilon_{r_2} \tag{2}$$

Lichetenecker model [16]:

$$\ln \varepsilon_r = (1-x)\ln \varepsilon_{r_1} + x \ln \varepsilon_{r_2} \tag{3}$$

where x is the volume fraction of TiO_2, ε_{r_1} and ε_{r_2} are the dielectric constant of LZP and TiO_2, respectively. The theoretical and measured dielectric constants of LZP–TiO_2 composites sintered at 950 °C for 4 h are described in Fig. 6. By comparing the experimentally observed values of ε_r with the predicted values, only Lichetenecker model is comparatively closer to the measured results. However, the theoretical value and experimental value exists a certain deviation. The deviation of ε_r from the predicted mixing relations may be due to not only the dissimilar microstructural grain morphologies of both phases but also the presence of porosity [17, 18].

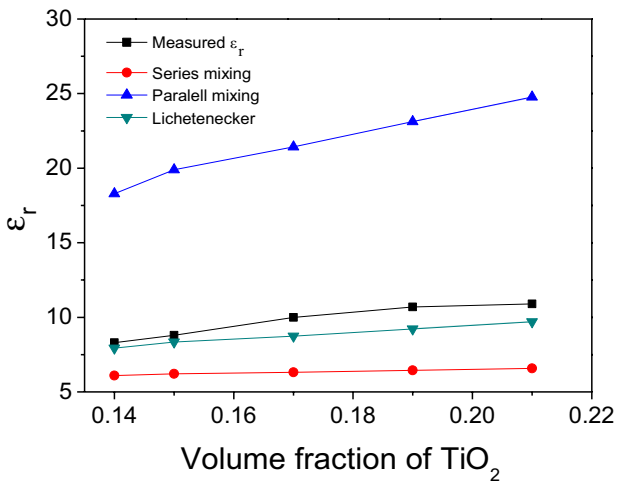

Fig. 6 Theoretical and measured dielectric constant of LZP–TiO_2 composites with different volume fraction of TiO_2 sintered at 950 °C for 4 h

Figure 7 shows the variation of experimental and calculated values of τ_f with the volume fractions of TiO_2. According to the Lichtenecker empirical rule [16], the value of τ_f for the composites can be predicted using the mixture rule:

$$\tau_f = v_1 \tau_{f_1} + v_2 \tau_{f_2} \tag{4}$$

where v_1 and v_1 are the volume fractions of LZP and TiO_2, τ_{f1} and τ_{f2} are the τ_f values of LZP and TiO_2, respectively. It is observed that both the theoretical τ_f values and the measured τ_f values increase with the increasing x value, and the change of the theoretical and measured τ_f values exhibits similar behavior. Clearly, a near zero τ_f value can

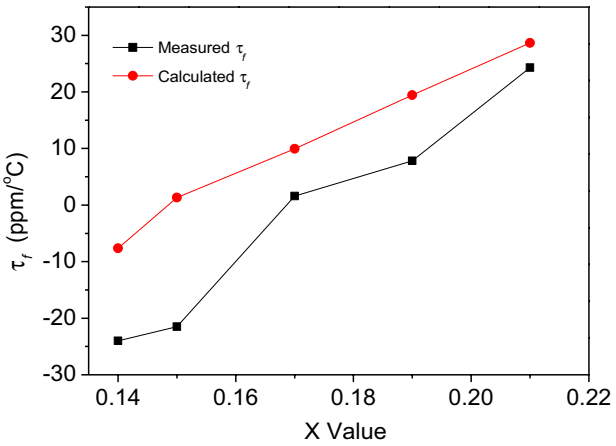

Fig. 7 Temperature coefficient of resonant frequency (τ_f) of $LiZnPO_4$-TiO_2 composite as a function of volume fraction of TiO_2

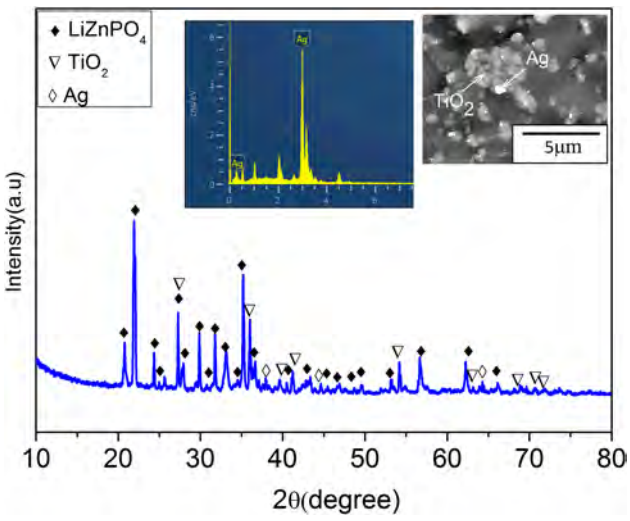

Fig. 8 XRD patterns of LZP −0.17 TiO_2 + 20 wt% Ag sintered at 900 °C for 4 h. The *insets* show the EDS and SEM image of this specimen

be obtained as x is in the vicinity of 0.17, as shown in Fig. 7 and Table 1. However, the theoretical τ_f and experimental τ_f exists a certain deviation, which may be due to the differences in crystal microstructure of LZP and TiO_2 phases.

Figure 8 depicts XRD patterns, EDS result and SEM profile of LZP −0.17 TiO_2 + 20 wt% Ag sintered at 900 °C for 4 h. From the XRD pattern, co-firing with Ag powders does not produce a new phase other than metallic silver, LZP (matrix) and TiO_2 in the sample. This observation is also confirmed by the SEM and EDS analysis (Fig. 8). The SEM analysis indicates no interaction forming new phases after firing, and it is obvious that the reaction of ceramics and Ag powders does almost not occur from the EDS result. Hence, this would benefit commercial applications in LTCC field.

4 Conclusions

LZP ceramic was fabricated through a solid-state reaction method. LZP ceramic fired at 850 °C for 4 h shows good dielectric properties of $\varepsilon_r = 5.3$, $Q \times f = 28{,}496$ GHz), and $\tau_f = -80.4$ ppm/°C. By adding TiO_2 in the LZP ceramic, the large negative value of τ_f can be facilely tune to near zero. Typically, the LZP + 0.17 TiO_2 (volume fraction) sintered at 950 °C for 4 h has $\varepsilon_r = 10.0$, $Q \times f = 10{,}025$ GHz, $\tau_f = 1.6$ ppm/°C. The merit for the TiO_2-added LZP ceramic is its good compatibility with the Ag electrode. These finding suggest the as-prepared ceramics could be a promising candidate for LTCC applications.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (Grant No. 51462005), the Research funds of The Guangxi Key Laboratory of Information Materials (Nos. 131018-Z and 131004-Z), Program for Postgraduate Joint Training Base (No. 20160513-14-Z) and Project supported by National Undergraduate Innovation Program of the Ministry of Education of China (1401010113).

References

1. B. Tang, X. Guo, S.Q. Yu, Z.X. Fang, S.R. Zhang, The shrinking process and microwave dielectric properties of $BaCu(B_2O_5)$-added $0.85BaTi_4O_9$–$0.15BaZn_2Ti_4O_{11}$ ceramics. Mater. Res. Bull. **66**, 163–168 (2015)
2. X. Tang, H. Yang, Q.L. Zhang, J.H. Zhou, Low-temperature sintering and microwave dielectric properties of $ZnZrNb_2O_8$ ceramics with $BaCu(B_2O_5)$ addition. Ceram. Int. **40**, 12875–12881 (2014)
3. G. Dou, D.X. Zhou, M. Guo, S.P. Gong, Low-temperature sintered Zn_2SiO_4-$CaTiO_3$ ceramics with near-zero temperature coefficient of resonant frequency. J. Alloys Compd. **513**, 466–473 (2012)
4. G.H. Chen, M.Z. Hou, Y. Yang, Microwave dielectric properties of low-fired Li_2TiO_3 ceramics doped with Li_2O–MgO–B_2O_3 frit. Mater. Lett. **89**, 16–18 (2012)
5. S.Y. Chung, J.T. Bloking, Y.M. Chiang, Electronically conductive phosphor-olivines as lithium storage electrodes. Nat. Mater. **1**, 123–128 (2002)
6. Q. Yu, H.D. Zeng, Q. Jiang, Z. Liu, L.Y. Sun, J. Ren, G.R. Chen, Preparation and luminescent properties of Mn^{2+} doped glass and glass-ceramics containing $LiZnPO_4$ nanocrystals. J. Non-Cryst. Solids **35**(4), 165–168 (2014)
7. C.M. OuYang, M.A. Shuai, Y. Rao, X. Zhou, X. Zhou, $LiZnPO_4$:Tb^{3+}, Ce^{3+}, green phosphors with high efficiency. J. Rare Earths **30**(7), 637–640 (2012)
8. X. Hu, Z.F. Cheng, Y. Li, Z.Y. Ling, Dielectric relaxation and microwave dielectric properties of low temperature sintering $LiMnPO_4$ ceramics. J. Alloys Compd. **651**, 290–293 (2015)
9. D. Thomas, M.T. Sebastian, Temperature-compensated $LiMgPO_4$: A new glass-free low-temperature cofired ceramic. J. Am. Ceram. Soc. **93**, 3828–3831 (2010)
10. J.A. Gard, G. Torres-Trevino, A.R. West, Crystal data for $LiZnPO_4$. J. Mater. Sci. Lett. **4**, 1138–1139 (1985)
11. D. Zhou, L.X. Pang, X. Yao, H. Wang, Influence of sintering process on the microwave dielectric properties of $Bi(V_{0.008}Nb_{0.992})O_4$ ceramics. Mater. Chem. Phys. **115**, 126–131 (2009)
12. G. Chen, M. Hou, Y. Bao, C.L. Yuan, C.R. Zhou, H.R. Xu, Silver co-firable $Li_2ZnTi_3O_8$, microwave dielectric ceramics with LZB glass additive and TiO_2 dopant. Int. J. Appl. Ceram. Technol. **10**(3), 492–501 (2013)
13. C.H. Hsu, H.A. Ho, Microwave dielectric in the $Sm(Co_{1/2}Ti_{1/2})O_3$–$CaTiO_3$ ceramic system with near-zero temperature coefficient with resonant frequency. Mater. Lett. **64**, 396–398 (2010)
14. D. Borrow, T. Petroff, R. Tandon, M. Sayer, Slab plasmon polaritons and waveguide modes in four-layer resonant semiconductor waveguides. J. Appl. Phys. **81**, 8761 (1997)
15. P. Sarah, S.V. Suryanarayana, Dielectric properties of piezoelectric 3–0 composites of lithium ferrite/barium titanate. Bull. Mater. Sci. **26**(7), 745–747 (2003)
16. K. Lichtenecker, Dielectric constant of natural and synthetic mixtures. Phys. Z 27(1926)115
17. H.H.B. Rocha, F.N.A. Freire, M.R.P. Santos, Radio-frequency (RF) studies of the magneto-dielectric composites: $Cr_{0.75}Fe_{1.25}O_3$(CRFO)-$Fe_{0.5}Cu_{0.75}Ti_{0.75}O_3$(FCTO). Phys. B **403**(17), 2902–2909 (2008)
18. D.W. Kim, H.J. Youn, K.S. Hong, C.K. Kim, Microwave dielectric properties of $(1\text{-}x)Ba_5Nb_4O_{15}$–$xBaNb_2O_6$ mixtures. Jpn. J. Appl. Phys. **41**, 3812–3816 (2002)