Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 1613–1617

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Glass-free low-temperature sintering and microwave dielectric properties of $CaWO_4$–Li_2WO_4 ceramics

Zhu Zhang, Hua Su*, Xiaoli Tang, Huaiwu Zhang, Tingchuan Zhou, Yulan Jing

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Received 16 May 2013; received in revised form 6 July 2013; accepted 10 July 2013
Available online 17 July 2013

Abstract

The microwave dielectric properties of $(1-x)\ CaWO_4-xLi_2WO_4$ ceramics prepared by the solid state reaction were investigated as a function of Li_2WO_4 content ($0\leq x\leq 0.14$). Due to the addition of Li_2WO_4 phase, the sintering temperature was reduced from 1150 °C to below the LTCC temperature limits. For the ceramics sintered at 900 °C and 950 °C, with the increase of x, the $Q\times f$ values first increased and then decreased. The density and permittivity presented the same behaviour as the $Q\times f$ values. At $x=0.1$, the $(1-x)CaWO_4-xLi_2WO_4$ ceramics sintered at 900 °C/2 h presented excellent microwave dielectric properties: $\varepsilon_r=9.002$, $Q\times f=11.76\times 10^4$ GHz and $\tau_f=-55$ ppm/°C. The ceramic was a chemically compatible with silver, which makes it a very promising candidate for LTCC application.

Keywords: Microwave dielectric properties; LTCC; $CaWO_4$–Li_2WO_4; Low loss

1. Introduction

Intensive development of wireless communication systems has resulted in an increasing demand for microwave dielectric materials with low dielectric constant and low loss materials. In addition, it is desired to integrate the passive components to a function module by low temperature co-fired ceramic (LTCC) technology. Materials with low sintering temperature (<960 °C), high quality factor ($Q\times f$) value and near zero temperature coefficient of resonant frequency (τ_f) are necessary for the applications [1–3]. Currently, reducing the sintering temperature without deteriorating the microwave properties is an arduous problem in LTCC material research. Low melting glass addition, chemical processing, and small particle size of starting materials are the three main methods normally used to reduce the sintering temperature of these dielectric ceramics. However, fine powders prepared by wet chemical processing such as the sol–gel process may complicate the fabrication process and increase the cost. Addition of low melting glass either leads to poor microwave dielectric properties or significantly increases the possibility of chemical reaction with the metal electrode due to the presence of complicated phases in the LTCC system [4,5]. In addition, glass addition can cause cracks during the soldering process due to the different thermal expansion coefficients between glasses and ceramic, especially when the glass addition amount is over 5 wt% [6,7].

Therefore, a glass-free LTCC material with low permittivity and appropriate microwave dielectric properties enables fabrication of devices for high speed applications [8,9]. Owing to their low permittivities (≤ 12) and high $Q\times f$ values ($>50{,}000$ GHz), the scheelite ceramics, with the general formula MWO_4 (M=Ca, Sr, and Ba) were regarded as promising materials for microwave substrate applications [10]. Previously, it was reported that $CaWO_4$ sintered at 1100 °C for 3 h exhibited a low ε_r (≈10) and a high $Q\times f$ value (≈75,000 GHz) [11]. Meanwhile, Li_2WO_4 presents excellent microwave dielectric properties ($Q\times f\approx 62{,}000$ GHz) and low melting point (≈741 °C) [12], which might promote the sintering of $CaWO_4$. In fact, Sung Joo Kim and Eung Soo Kim have investigated the effects of Li_2WO_4 on the microwave dielectric properties of $0.85CaWO_4$–$0.15SmNbO_4$ ceramics as a sintering additive, but not the effects as a second phase [13].

In this paper, we investigated the sintering behavior and microwave dielectric properties of $(1-x)CaWO_4-xLi_2WO_4$ to obtain a new glass-free LTCC material.

*Corresponding author. Tel.: +86 2883203793.
E-mail address: uestcsh@163.com (H. Su).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.07.050

2. Experimental procedure

WO_3 (99%), $CaCO_3$ (99.9%) and Li_2CO_3 (99%) were used as starting materials. The powders were weighed according to the formula of $(1-x)CaWO_4-xLi_2WO_4$ ($0\le x\le 0.14$), and milled with ZrO_2 balls in distilled water for 12 h. The mixtures were dried and calcined at the temperature of 800 °C for 2 h. The calcined powders were reground for 12 h, then dried and mixed with 15 wt% PVA as binder and granulated. The granulated powders were uni-axially pressed into pellets with 12 mm in diameter and 5–6 mm in height under the pressure of 10 MPa. The pellets were sintered at the temperature ranging from 850 °C to 950 °C for 2 h with heating rate of 5 °C/min.

The crystalline phases of the sintered ceramics were analyzed by X-ray diffraction (XRD: DX-2700) using Cu K_α radiation. The micrographs were obtained by using scanning electron microscope SEM (SEM: INCA penta FETX3 oxford). The bulk density was measured by the Archimedes method. The microwave dielectric properties of the sintered samples were evaluated by the Hakki–Coleman method and Agilent N5230A (300 − 20 GHz) network analyzer in a resonant cavity. The temperature coefficient resonant frequency (τ_f) was also measured by the same method in a temperature ranging from 20 °C to 80 °C and calculated from the following equation: $\tau_f=(f_{80}-f_{20})/[f_{20}\times(80-20)]\times 10^6$ (ppm/°C), where f_{80} and f_{20} represent the resonant frequency at 80 °C and 20 °C, respectively. The chemical compatibility with silver was investigated by co-firing the mixed powders with pure silver powders (20 wt % Ag) in ambient atmosphere at 900 °C for 2 h.

3. Results and discussion

Fig. 1 shows the XRD patterns of $(1-x)\ CaWO_4-xLi_2WO_4$ ($0\le x\le 0.14$) samples sintered at 900 °C for 2 h. All Li_2WO_4 added samples exhibited $CaWO_4$ (PDF #41-1431) main phase with trace amount of Li_2WO_4 (PDF #12-0760) phase. It was speculated that the Li_2WO_4 phase could coexist with $CaWO_4$ phase in the $(1-x)\ CaWO_4-xLi_2WO_4$ system. $CaWO_4$ belonged to the tetragonal scheelite system (space group $I4_1/a$ (No. 88)) [14], and the lattice parameters are $a=b=0.524$ nm, $c=1.138$ nm. Li_2WO_4 belonged to the rhombohedral phenacite structure (space group $R\bar{3}$ (No. 148)) [12], and the lattice parameters are $a=b=1.436$ nm, $c=0.960$ nm. And, it was observed that the intensities of diffraction peaks of the Li_2WO_4 phase increased gradually with the increase in proportion of Li_2WO_4 in the compounds.

The SEM micrographs of $(1-x)CaWO_4$–xLi_2WO_4($0\le x\le 0.14$) ceramics sintered at 900 °C for 2 h in air are shown in Fig. 2. The photos indicated that grain size became enlarged with increasing Li_2WO_4. However, the grains first gradually became denser with the increase of x from 0 to 0.1, and then abnormal grain growth and defects gradually increased with x of more than 0.12, which was mainly attributed to the excessive liquid phase of Li_2WO_4.

Fig. 3 shows the $Q\times f$ values of $(1-x)CaWO_4-xLi_2WO_4$ ($0.06\le x\le 0.14$) ceramics sintered at 850 °C, 900 °C and 950 °C for 2 h in air. With the increase of Li_2WO_4 content, the optimal sintering temperature gradually decreased. This was due to the low melting point of Li_2WO_4. When the sintering temperature was at 850 °C, the $Q\times f$ values of $(1-x)CaWO_4-xLi_2WO_4$ ($0.06\le x\le 0.14$) ceramics clearly increased but not yet saturated. However, when the ceramics sintered at 900 °C and 950 °C, with the increase of x, the $Q\times f$ value increased to a maximum and then decreased. This might be related to the density of the samples. As shown in Figs. 2 and 3, we could see that the $Q\times f$ values had roughly the same trend as the density. This could be related to the abnormal grain growth, which results in more pores. It is known that the microwave dielectric loss includes the intrinsic and the extrinsic losses [2]. The intrinsic losses are dependent on the crystal structure and mainly caused by lattice vibration modes [15], while the extrinsic losses are associated with many factors, such as impurities, microstructural defects, densification or porosity, grain size, second phase, presence of liquid-phase or grain boundaries [16]. Therefore, our results might become apparent because extrinsic factors play a major role, especially the porosity.

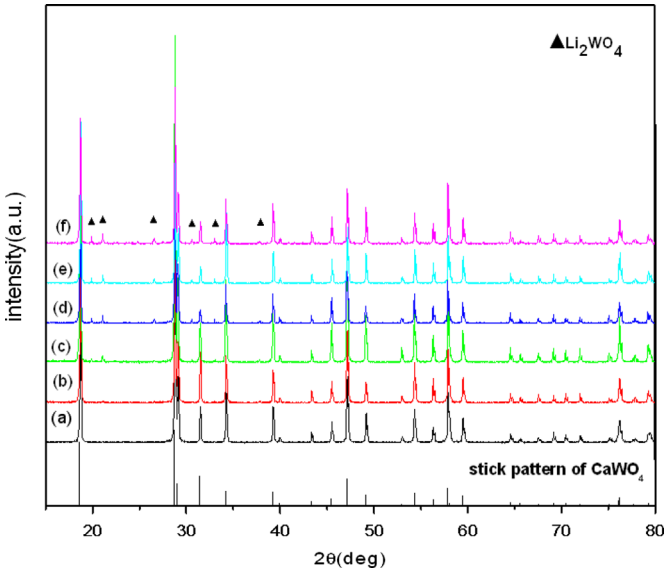

Fig. 1. XRD patterns of $(1-x)CaWO_4$–xLi_2WO_4 ceramics (a) $x=0$, (b) $x=0.06$, (c) $x=0.08$, (d) $x=0.10$, (e) $x=0.12$, and (f) $x=0.14$ sintered at 900 °C for 2 h in air.

The changes in relative density and permittivity of $(1-x)\ CaWO_4-xLi_2WO_4$ ($0.06\le x\le 0.14$) ceramics sintered at 850 °C, 900 °C and 950 °C for 2 h in air are shown in Figs. 4 and 5. As expected, permittivity closely followed density in all cases. It could be seen that the relative density of the samples clearly increased with the increase of Li_2WO_4 content, when the sintering temperature was at 850 °C. However, when the samples were sintered at 900 °C and 950 °C, with the increase of Li_2WO_4 content, the relative density increased to a maximum and then decreased. The ceramic sample had a relative density above 97%. As shown in Fig. 2, the SEM photos show that the increase in porosity with x of more than 0.12 lead to deteriorated density. Also, the calculated density of the sample was obtained by the following equations [17]:

$$\rho=\frac{w1+w2}{w1/\rho1+w2/\rho2} \quad (1)$$

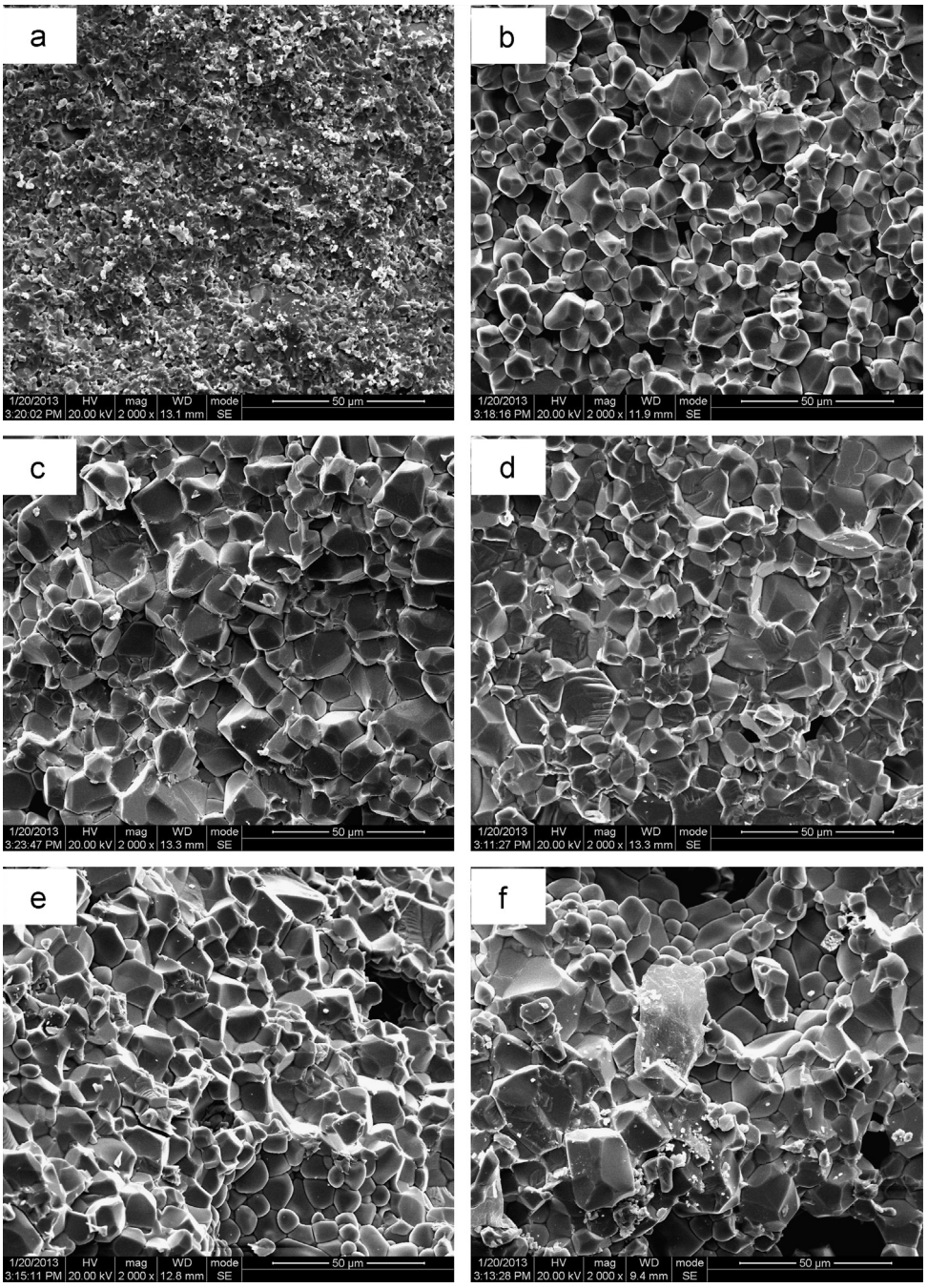

Fig. 2. SEM micrographs of $(1-x)CaWO_4$–xLi_2WO_4 ceramics. (a) $x=0$, (b) $x=0.06$, (c) $x=0.08$, (d) $x=0.10$, (e) $x=0.12$, and (f) $x=0.14$ sintered at 900 °C for 2 h in air.

Where ρ_1 and ρ_2 are the theoretical density of $CaWO_4$ and Li_2WO_4, w_1 and w_2 are the weight fraction of $CaWO_4$ and Li_2WO_4. Therefore, with the increase of Li_2WO_4 content, the density of the compound decreased, as Li_2WO_4 was less dense than $CaWO_4$. The similar behavior of permittivity and density indicated that the permittivity was significantly affected by the density.

Fig. 6 shows the τ_f values of $(1-x)CaWO_4-xLi_2WO_4$ $(0.06\leq x\leq 0.14)$ ceramics sintered at 900 °C for 2 h in air. It could be seen that the τ_f values were all negative. This could be overcome by adding a positive τ_f material. As the Li_2WO_4 content increases, the absolute value of τ_f increased. This result was different from the report [13] that τ_f increased to the positive value when Li_2WO_4 acting as a sintering additive only. In a composite ceramic system, τ_f of the samples can be calculated by the following equations [18]:

$$\tau_f = V_1\tau_{f1} + V_2\tau_{f2} \quad (2)$$

Where V_1 and V_2 are the volume fraction of $CaWO_4$ and Li_2WO_4, τ_{f1} and τ_{f2} are the τ_f values of $CaWO_4$ and Li_2WO_4 phase, respectively. $CaWO_4$ had a higher τ_f of -53 ppm/°C [19], while Li_2WO_4 had a lower τ_f of -146 ppm/°C [12].

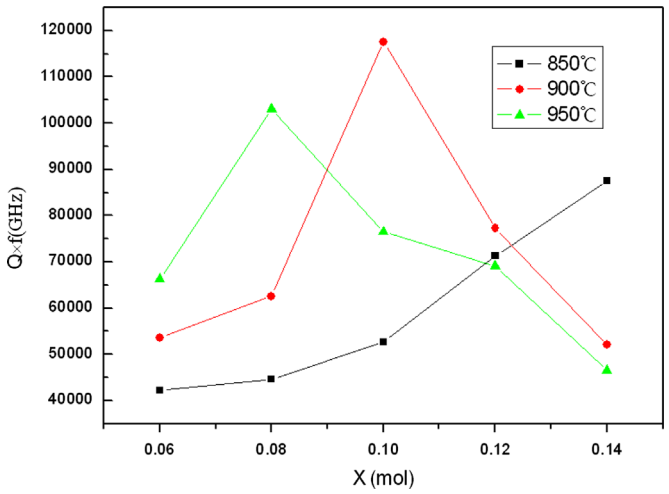

Fig.3. The $Q \times f$ of $(1-x)CaWO_4-xLi_2WO_4$ ($x=0.06$, $x=0.08$, $x=0.10$, $x=0.12$, $x=0.14$) ceramics sintered at 850 °C, 900 °C and 950 °C for 2 h in air.

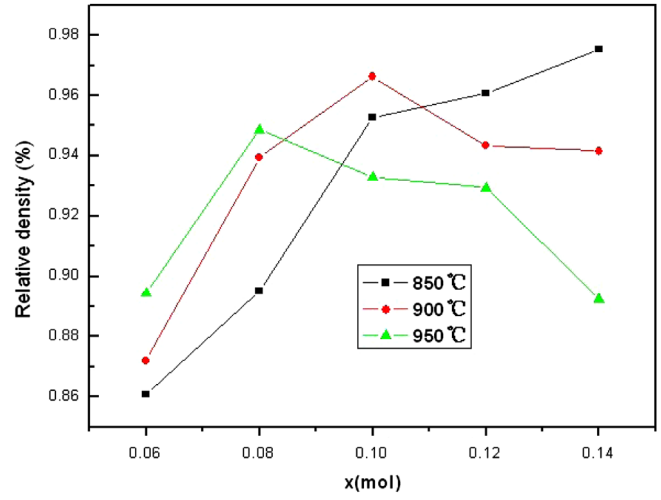

Fig. 4. The relative density of $(1-x)CaWO_4$–xLi_2WO_4 ($0.06 \le x \le 0.14$) ceramics sintered at 850 °C, 900 °C and 950 °C for 2 h.

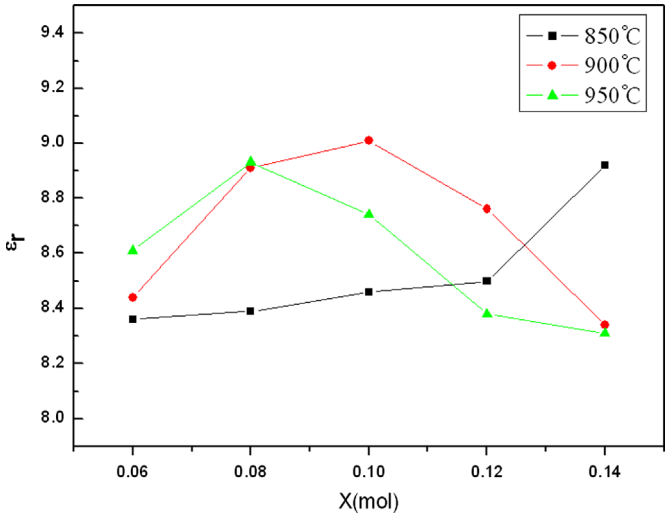

Fig. 5. The permittivity of $(1-x)CaWO_4$–xLi_2WO_4 ($0.06 \le x \le 0.14$) ceramics sintered at 850 °C, 900 °C and 950 °C for 2 h.

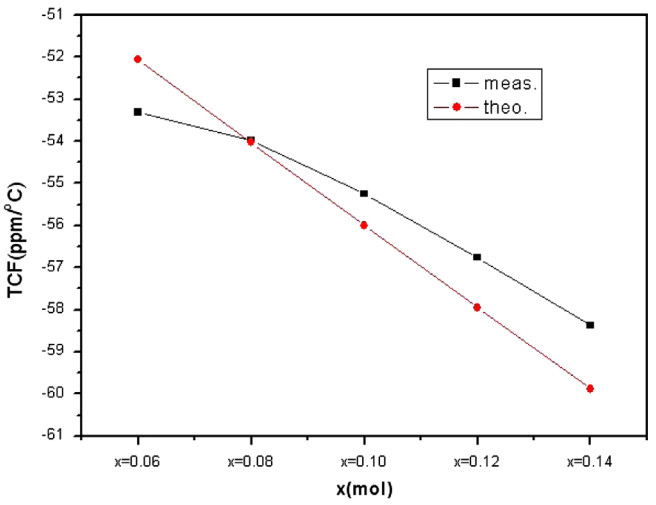

Fig. 6. The τ_f of $(1-x)CaWO_4-xLi_2WO_4$ ($0.06 \le x \le 0.14$) ceramics sintered at 900 °C for 2 h in air.

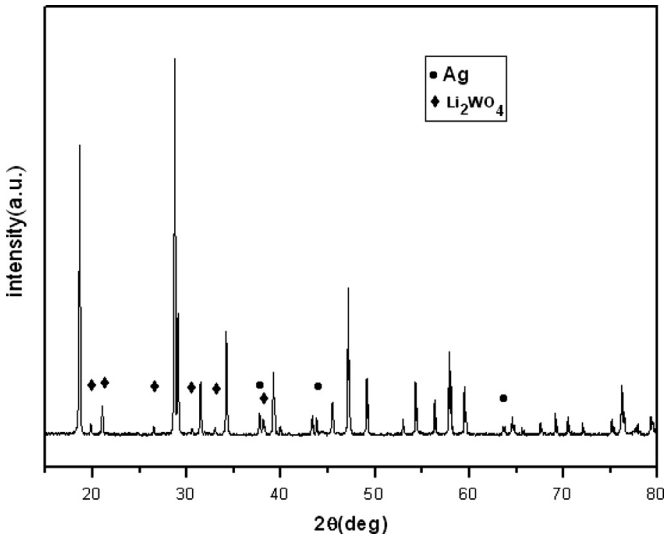

Fig. 7. Powder XRD pattern of $0.9CaWO_4-0.1Li_2WO_4$ mixed with 20 wt% Ag powders sintered at 900 °C for 2 h in air.

The theoretical τ_f value of the sample decreased with the increasing Li_2WO_4 content. Similarly, the measured τ_f value of the sample also decreased with increasing Li_2WO_4 content.

Fig. 7 shows the XRD pattern of the $0.9CaWO_4-0.1Li_2WO_4$ mixed with 20 wt% Ag powers sintered at 900 °C/2 h in air. All the major peaks of Ag were observed in the XRD pattern and no phase of silver compounds presented. It seems to show that no chemical reaction has taken place between the $0.9CaWO_4-0.1Li_2WO_4$ ceramic and Ag.

4. Conclusion

$CaWO_4$ ceramics modified with Li_2WO_4 were investigated as a promising microwave dielectric material for LTCC applications. All the samples exhibited $CaWO_4$ main phase with trace amount of Li_2WO_4 phase. The Li_2WO_4 reduced the sintering temperature and the microwave dielectric loss. All samples exhibited negative τ_f values. High performance of microwave dielectric properties were

obtained in the $0.9CaWO_4-0.1Li_2WO_4$ ceramics sintered at 900 °C with a microwave permittivity of 9.002, $Q\times f=11.76\times 10^4$ GHz and $\tau_f=-55$ ppm/°C. The ceramic was a chemically compatible with silver, which makes it a very promising candidate for LTCC application.

Acknowledgment

This work was supported by the National Natural Science Foundation of China under Grant nos. 61171047, 51132003, 51072029 and 61271038, and Program for New Century Excellent Talents in University, and Science and Technology Department of Sichuan Province.

References

[1] Jing Guo, Di Zhou, Hong Wang, Xi Yao, Microwave dielectric properties of $(1-x)ZnMoO_4-xTiO_2$ composite ceramics, Journal of Alloys and Compounds 509 (2008) 5863–5865.

[2] Mei Guo, Gang Dou, Shuping Gong, Dongxiang Zhou, Low-temperature sintered $MgWO_4$–$CaTiO_3$ ceramics with near-zero temperature coefficient of resonant frequency, Journal of the European Ceramic Society 32 (2012) 883–890.

[3] Li-Xia Pang, Di Zhou, Jing Guo, Ze-Ming Qi, Tao Shao, Microwave dielectric properties of scheelite structured low temperature fired $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic, Ceramics International 39 (2013) 4719–4722.

[4] M. Valant, D. Suvorov, Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates, Journal of the European Ceramic Society 24 (2004) 1715–1719.

[5] M. Valant, D. Suvorov, Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20-\delta}$ (M=Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$), Journal of the American Ceramic Society 84 (2001) 2900–2904.

[6] J.J. Bain, D.W. Kim, K.S. Hong, Glass-free LTCC microwave dielectric ceramics, Materials Research Bulletin 40 (2005) 2120–2129.

[7] G. Subodh, M.T. Sebastian, Glass-free $Zn_2Te_3O_8$ microwave ceramic for LTCC applications, Journal of the American Ceramic Society 90 (2007) 2266–2268.

[8] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, International Materials Review 53 (2008) 57–90.

[9] Nai Xian Wu, Jian Jiang Bian, Glass-free low-temperature co-fired ceramics microwave ceramic $AW_{1-x}Te_xO_4$ (A=Ca, Sr, Zn), International Journal of Applied Ceramic Technology 8 (2011) 1494–1500.

[10] Marjeta Maček Kržmanc, Manca Logar, Bojan Budič, Danilo Suvorov, Dielectric and Microstructural Study of the $SrWO_4$, $BaWO_4$, and $CaWO_4$ Scheelite Ceramics, Journal of the American Ceramic Society 94 (2011) 2464–2472.

[11] E.S. Kim, S.H. Kim, B.I. Lee, Low-temperature sintering and microwave dielectric properties of $CaWO_4$ ceramics for LTCC applications, Journal of the European Ceramic Society 26 (2006) 2101–2104.

[12] Clive A Di Zhou, Li-Xia Randall, Hong Pang, Jing Wang, Gao-Qun Guo, Xin-Guang Zhang, Li Wu, Shui, Xi Yao, Microwave dielectric properties of Li_2WO_4 ceramic with ultra-low sintering temperature, Journal of the American Ceramic Society 94 (2011) 348–350.

[13] Sung Joo Kim, Eung Soo Kim, Microwave dielectric properties of $0.85CaWO_4$–$0.15SmNbO_4$ ceramics with sintering additives, Ceramics International 35 (2009) 137–141.

[14] Park Il Hwan, Kim Beom-Soo, Kim Kyung-Yong, Kim Byong-Ho, Microwave dielectric properties and mixture behavior of $CaWO_4$–Mg_2SiO_4 ceramics, Japanese Journal of Applied Physics 40 (2001) 4956–4960.

[15] V.L. Gurevich, A.K. Tagantsev, Intrinsic dielectric loss in crystals, Advances in Physics 40 (1991) 719–767.

[16] S.J. Penn, N.M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, et al., Effect of porosity and grain size on the microwave dielectric properties of sintered alumina, Journal of the American Ceramic Society 80 (1997) 1885–1888.

[17] Zhenxing Hao Zhuang, Fei Yue, Jing Zhao, Longtu Pei, Li, Microstructure and microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ composite ceramics, Journal of Alloys and Compounds 472 (2009) 411–415.

[18] A.E. Paladino, Temperature-compensated $MgTi_2O_5$–TiO_2 dielectrics, Journal of the American Ceramic Society 54 (1971) 168–169.

[19] Sung Hun Yoon, Dong-Wan Kim, Seo-Yong Cho, Kug Sun Hong, Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds, Journal of the European Ceramic Society 26 (2006) 2051–2054.