Journal of
Ceramic Science
and Technology

J. Ceram. Sci. Technol., 09 [4] 471-476 (2018)
DOI: 10.4416/JCST2018-00034
available online at: http://www.ceramic-science.com

Short Communication

Novel Low-Permittivity, Low-Sintering-Temperature Na_2WO_4 Microwave Dielectric Ceramics for LTCC Applications

H.L. Dong[1, 3], C.X. Hu[*1, 2], W.J. Wang[2], H.P. Bao[3], W.J. Liu[2], B. Yang[1, 4]

[1]School of Science, Xijing University, Xi'an 710123, China
[2]Faculty of Science, Xi'an Aeronautical University, No. 259, West 2nd Ring, Xi'an, 710077, China.
[3]School of Physics and Electronic Information Engineering,
Qinghai Nationalities University, Xining 810007, China
[4]Surface and Interface Science Laboratory, RIKEN 2 – 1 Hirosawa, Wako-shi, Saitama 351 – 0198, Japan
received April 15, 2018; received in revised form July 4, 2018; accepted July 23, 2018

Abstract

A novel Na_2WO_4 ceramic with low sintering temperature was successfully synthesized by means of the reactive sintering process. The phase composition, microstructure and microwave dielectric properties of the Na_2WO_4 dielectric ceramic with different sintering temperature (600, 650, 680 and 700 °C) were investigated in detail using X-ray diffraction (XRD), scanning electron microscopy (SEM) and a vector network analyzer, respectively. Excellent microwave dielectric properties with a relative permittivity (ε_r) ~ 3.45, a quality factor (Q×f) ~ 38 244 GHz (at 13.64 GHz) and a temperature coefficient of resonant frequency (τ_f) ~ -42 ppm/K was obtained at a sintering temperature of 680 °C for 2 h. The results indicate that the Na_2WO_4 ceramic is a promising candidate for low-temperature co-fired ceramic technology.

Keywords: Microwave dielectric properties, low sintering temperature, Na_2WO_4, reactive sintering process

I. Introduction

Microwave dielectric materials with light weight, low cost, high dielectric constant and low loss have been widely applied in the ever-growing wireless communication and microwave circuits, such as dielectric resonators, filters, diplexers, antennas, oscillators and smart phones [1–3]. Low-temperature-sintered ceramics with a high quality factor (Q×f), an appropriate dielectric constant (ε_r), and a near-zero temperature coefficient of resonant frequency (τ_f) have attracted much interest in low-temperature co-fired ceramics (LTCC) applications [4–8]. Meanwhile a large number of low-temperature-sintered materials with excellent microwave dielectric properties have been reported, such as glasses and glass-ceramics, vanadate ceramics, tungstate ceramics, molybdate ceramics, tellurate ceramics and borate ceramics [8]. Recently, tungstate ceramics have been favored by researchers because of their low dielectric constant, low loss, and ultra-low sintering temperature. Bowen Zhang et al. obtained excellent microwave dielectric properties with a ε_r of 10.69, a Q×f value of 20 000 GHz (at 10 GHz) and a τ_f value of -35 ppm/K for $0.97CoWO_4$-0.03CuO sintered at 950 °C with the use of CuO to modify the $CoWO_4$ ceramics [1]. Di Zhou et al. reported that the Li_2WO_4 ceramic with phenacite structure can be sintered effectively at 640 – 660 °C with the solid-state reaction method, and obtained a ε_r of 5.5, a Q×f value of 62 000 GHz and a τ_f value of -146 ppm/K at 15.7 GHz [9]. Jie Li et al. reported a Li_4WO_5 low-firing ceramic with rock salt structure and excellent microwave dielectric properties with a near-zero temperature coefficient of resonant frequency ~ -2.6 ppm/K, a relative permittivity ~ 8.6 and a quality factor ~23 100 GHz (at 11.0 GHz) [10]. Huanfu Zhou et al. studied the microwave dielectric properties of $LiBiW_2O_8$ ceramics with low sintering temperature, the results indicate that $LiBiW_2O_8$ ceramic with a ε_r of 26.5, a Q×f value of 16 400 GHz, and a τ_f value of 70 ppm/K could be prepared at 700 °C for 2 h [11]. Liang Fang et al. obtained the low-firing $Li_2Mg_2W_3O_{12}$ (ε_r ~ 8.4, Q×f ~ 56 700 GHz, τ_f ~ -72.8 ppm/K) and $Li_2Zn_2W_3O_{12}$ (ε_r ~ 11.3, Q×f ~ 24 500 GHz, τ_f ~ -100 ppm/K) ceramics at 720 and 700 °C, respectively [12]. Other tungstate ceramics are summarized in Table 1.

Despite the discoveries of the above-mentioned new classes of microwave dielectric ceramics with ultra-low sintering temperature, the development of such or similar materials with the required high performance is still a highly challenging task, particularly the unreported Na_2WO_4 ceramic at present. In this work, a novel microwave substrate Na_2WO_4 ceramic was synthesized with the reactive sintering process. Furthermore, the effects of sintering temperature on phase composition, microstructure and microwave dielectric properties were systematically investigated.

* Corresponding author: huchengxi@163.com

Table 1: Comparison of microwave dielectric properties of some tungstate ceramics with microwave dielectric permittivity from No. 5 to No. 15.

No.	Samples	S_T (°C)	F (GHz)	ε_r	Q×f (GHz)	τf (ppm/K)	Ref.
1		600	13.7	3.4	13 637	-36.5	
2	Na_2WO_4	650	13.7	3.3	16 190	-42.1	This
3		680	13.6	3.5	38 244	-42.1	work
4		700	13.7	3.7	27 049	-48.9	
5	$0.97CoWO_4$-0.03CuO	950	10	10.7	20 000	-35	[1]
6	Li_2WO_4	650	15.7	5.5	62 000	-146	[9]
7	Li_4WO_5	890	11	8.6	23 100	-2.6	[10]
8	$LiBiW_2O_8$	700	6–7	26.5	16 400	-70	[11]
9	$Li_2Zn_2WO_4$	700	-	11.3	24 500	-100	[12]
10	$Li_2Mg_2WO_4$	720	-	8.4	56 700	-73	[12]
11	$Li_2Mg_2W_2O_9$	820	11	10.3	20 537	-76.9	[17]
12	$CaWO_4$-$2Li_2WO_4$	740	10–13	6.1	62 400	-100.1	[18]
13	$PbWO_4$	620	7.0	21.4	43 000	-7	[19]
14	Pb_2WO_4	520	7.6	16.4	14 800	-95	[19]
15	$(Ag, Bi)_{0.5}WO_4$	580	7.5	35.9	13 000	-69	[20]

S_T sintered temperature; F resonant frequency.

II. Experimental

The Na_2WO_4 ceramic materials were prepared with the reactive sintering method using proportionate amounts of raw materials: Na_2CO_3 (≥ 99.8 %, Sinopharm Chemical Reagent Co., Ltd, Beijing, China) and WO_3 (≥ 99.0 %, Sinopharm Chemical Reagent Co., Ltd, Beijing, China). The starting materials were accurately weighed based on molar ratios and ball-milled in alcohol solution with ZrO_2 balls for 8 h, and then dried for 24 h. The as-dried powders were mixed with 5 wt% polyvinyl alcohol (PVA) for granulation. The granulated powders were pressed into cylindrical compacts with a diameter of 10 mm and thickness of 5 mm under uniaxial pressure of 220 MPa. Finally, the manufactured green bodies were placed into an alumina crucible and sintered in a temperature range from 600 to 700 °C for 2 h in air atmosphere with a heating rate of 5 K/min, and then cooled down naturally to room temperature inside the furnace.

The structure of the crystalline phase for the as-fabricated Na_2WO_4 ceramic was identified by means of X-ray diffraction (XRD: D/max-2550V/PC, Rigaku, Japan) with CuKα radiation (λ = 1.5406 Å) at a scanning speed of 10 °·min^{-1} with 40 kV and 100 mA in the 2θ range of 10–80°. The microstructure of the as-prepared specimens was observed by means of scanning electron microscopy (SEM: FEI-quanta 200, USA). The bulk density of the as-produced samples was measured with the Archimedes method using distilled water as the medium on an electronic balance (Model: XT220A, Precisa, Switzerland) with 0.0001 g precision. A vector network analyzer (ZVB20, Rohde & Schwarz, Germany) was used to test the microwave dielectric properties of the as-fabricated ceramics with the $TE_{01\delta}$ shielded cavity method in the frequency range of 9–14 GHz. The temperature coefficients of τ_f were tested at temperatures ranging from 25 to 80 °C. τ_f was calculated by the following equation:

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \cdot (80 - 25)} \cdot 10^6 \text{ (ppm/K)}$$

where f_{25} and f_{80} are the $TE_{01\delta}$ resonant frequency at 25 and 80 °C, respectively.

III. Results and Discussion

Fig. 1 shows the room-temperature XRD patterns of the Na_2WO_4 ceramic sintered at 600–700 °C for 2 h. The

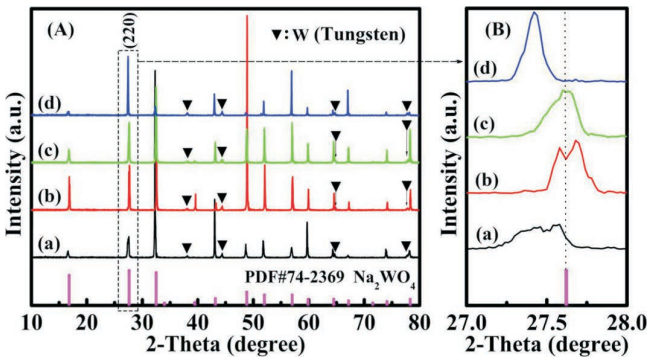

Fig. 1: XRD patterns of Na_2WO_4 ceramic sintered at different temperature for 2 h, (a) 600 °C, (b) 650 °C, (c) 680 °C, (d) 700 °C.

Na_2WO_4 phase with a cubic structure belonging to the Fd-3m (227) space group was obtained, but the XRD display also contains some peaks, which was indexed to tungsten (W). The enlarged XRD patterns of the strongest peak ((220) crystal face) in Fig. 1A at the range of 2θ from 27 to 28° are depicted in Fig. 1B. With the increase in sintering temperature, the location of the XRD patterns of the Na_2WO_4 ceramic shifted to a lower angle. This indicates that the interplanar spacing (D value) of as-prepared Na_2WO_4 ceramic increased gradually with the rise in sintering temperature.

Fig. 2 presents the SEM images on the surface of Na_2WO_4 ceramic sintered at different temperatures for 2 h. It could be observed that the grains of the Na_2WO_4 ceramis gradually formed and grew with the increase in sintering temperature from 600 to 700 °C, and more and more grains could be also observed, especially in the sample sintered at 700 °C. It is clear that uniform and dense grain morphology could be observed in the SEM image of the ceramics sintered at 650 °C (Fig. 2b). The ceramic sintered at 680 °C for 2 h had a dense structure with a fine wavy line size (Fig. 2c). The increase in pores with the sintering temperature (as seen in Fig. 2d) induces the bulk density and the microwave dielectric properties of the ceramics. In order to confirm the compositional difference between two types of grains, composition analysis was performed by means of EDS on the particulate (Spot B) and non-particulate (Spot A) of the Na_2WO_4 samples sintered at 680 °C for 2 h (Fig. 2c), and the results are shown in the inset. The ratio of W:Na:O of Spot A is 37.50:36.45:26.05, which was not close to 1:2:4, indicating Spot A was a mix of W phase and Na_2WO_4 phase with the chemical composition of Na_2CO_3-WO_3. Conversely, the ratio of W:Na:O of Spot B is 20.87:40.44:38.69, which is approximately consistent with composition of Na_2WO_4. The EDS analysis of both Spot A and Spot B agreed with the XRD patterns in Fig. 1.

Fig. 3 illustrates the variation of bulk density of Na_2WO_4 ceramics prepared at different sintering temperature. With the increase in sintering temperature, the bulk density of the specimens increased at first and then decreased slightly. The Na_2WO_4 sample sintered at an optimum temperature of 650 °C for 2 h exhibits a maximum experimental density of 4.49 g/cm^3, which corresponds to 88 % of the theoretical density (5.13 g/cm^3). Therefore, the optimum densification sintering temperature of the Na_2WO_4 ceramics was considered to be 650 °C for 2 h.

Fig. 4 shows the variations in the values of ε_r, Q×f and τ_f of as-prepared Na_2WO_4 ceramics as a function of sintering temperature. The dielectric constant is dependent on the density, dielectric polarizabilities, and structural character such as the distortion, tilting, and rattling spaces of the oxygen octahedron in the unit cell [13, 14]. Generally, the dielectric permittivity should increase with

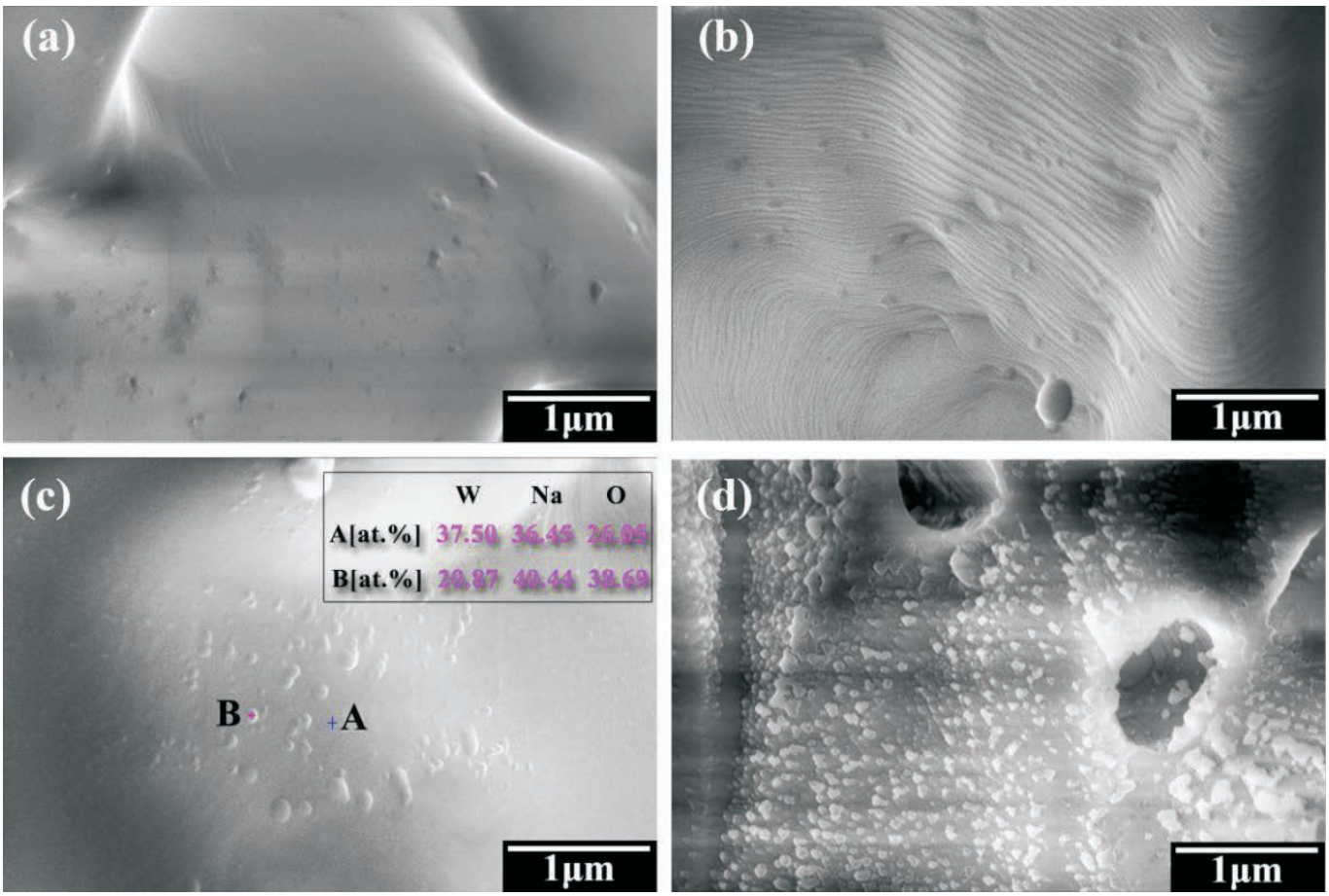

Fig. 2: SEM images of Na_2WO_4 ceramic sintered at different temperature for 2 h, (a) 600 °C, (b) 650 °C, (c) 680 °C, (d) 700 °C.

increasing density, but in our study, the opposite was observed (Fig. 4a); this result is similar to that in Reference [15]. On the basis of the XRD and SEM analysis, it could be determined that the formation temperature of the grains in Na_2WO_4 ceramics was higher than 650 °C. Consequently, crystallization plays a critical role in the variation of the dielectric constant.

It has been reported that Q×f values at microwave frequencies depend on intrinsic and extrinsic factors, such as densification, impurities, substitution, grain boundaries, grain morphology and shape, secondary phase, pores, and so on [16]. Fig. 4b exhibits the change of the Q×f value at different sintering temperatures, with this increasing clearly from 13 637 GHz at 600 °C to 38 244 GHz at 13.64 GHz at 680 °C, indicating that increasing sintering temperature can assist in enhancing the Q×f value of Na_2WO_4 ceramics. However, the Q×f value decreases with further increase in the sintering temperature, falling to 27 049 GHz at 700 °C.

The τ_f values of Na_2WO_4 samples sintered at varying temperature from 600 to 700 °C are shown in Fig. 4c. It can be seen that the τ_f value decreased gradually from -36.5 to -49.0 ppm/K with increasing sintering temperature, indicating that the τ_f values of Na_2WO_4 ceramics should be adjusted to near zero with a composite or by adopting positive τ_f for practical application in the future.

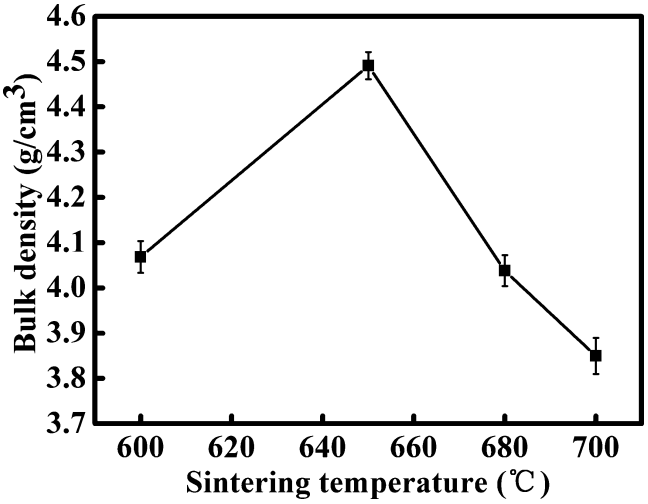

Fig. 3: Bulk density of the specimens sintered at varying temperature for 2 h.

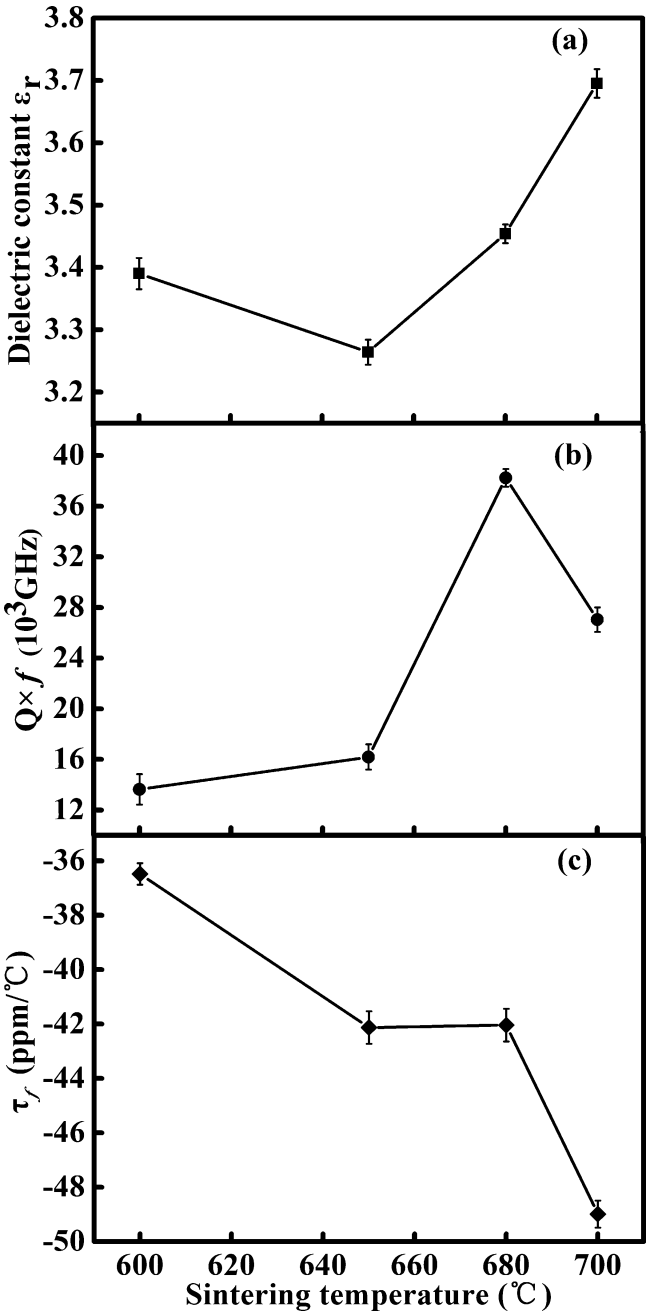

Fig. 4: The ε_r, Q×f, and τ_f values of Na_2WO_4 ceramic sintered at varying temperature for 2 h.

The literature work and the current work were compared as shown in Table 1. It can be seen that Na_2WO_4 ceramic is advantageous compared to other materials with regard to its low dielectric relative permittivity ε_r, low dielectric loss and high Q×f values after ultra-low temperature synthesis, which is a necessary requirement for microwave dielectric substrate applications. However, the ε_r and Q×f values of Na_2WO_4 ceramics can be improved based on this study with the modified technology process, for example, with the conventional solid-state reaction method. Meanwhile its large negative τ_f values should be improved to near zero before application via a method of solid solution and composites.

IV. Conclusions

The cubic structure Na_2WO_4 ceramic was prepared with the reactive sintering method using Li_2CO_3 and WO_3 powder as raw materials. The excellent microwave dielectric properties with a relative permittivity ε_r of 3.45, a quality factor Q×f of 38 244 GHz (at 13.64 GHz) and a temperature coefficient of resonant frequency τ_f of -42.0 ppm/K were obtained after sintering at 680 °C for 2 h. The analytical results show that Na_2WO_4 ceramic is a promising candidate for low-temperature ceramic technology.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was financially supported by the Provincial International Technology Cooperation Project of Qinghai, China (No. 2015-HZ-811), and the National Natural Science Foundation of China (Grant No. 51402235,51272150,11064011).

References

1 Zhang, B., Li, L.X.: Microstructure and microwave dielectric properties of CuO-modified $CoWO_4$ ceramics, J. Mater. Sci. Mater. El., **27**, 1 – 7, (2016).

2 Zhang, P., Liu, L., Zhao, Y.G., Xiao, M.: Low temperature sintering and microwave dielectric properties of $Li_3Mg_2NbO_6$ ceramics for LTCC application, J. Mater. Sci. Mater. El., **28**, 5802 – 5806, (2017).

3 Hu, C.X., Liu, Y., Liu, P., Zhang, W.W., Zhu, J.R.: Microwave dielectric properties of (1-x)SiO_2-xTiO_2 composite ceramics derived from core-shell structured microspheres, Mater. Res. Bull., **53**, 54 – 57, (2014).

4 Lin, Y.L., Wang, S.F., Lai, B.C., Liu, Y.X., Chang, Y.L.: Densification, microstructure evolution, and microwave dielectric properties of $Mg_{1-x}Ca_xZrTa_2O_8$ ceramics, J. Eur. Ceram. Soc., **37**, 2825 – 2831, (2017).

5 Hu, C.X., Liu, P.: Preparation and microwave dielectric properties of SiO_2 ceramics by aqueous sol-gel technique, J. Alloy. Compd., **559**, 129 – 133, (2013).

6 Niu, Y.J., Liu, M.T., Li, M.F., Bi, J.X., Wu, H.T.: Influence of Mg^{2+} substitution on the crystal structure and microwave dielectric properties of $ZnZrNb_2O_8$ ceramics, J. Alloy. Compd., **705**, 399 – 404, (2017).

7 Neelakantan, U.A., Kalathil, S.E., Ratheesh, R.: Structure and microwave dielectric properties of ultralow-temperature cofirable BaV_2O_6 ceramics, Eur. J. Inorg. Chem., **2015**, 305 – 310, (2015).

8 Sebastian, M.T., Wang, H., Jantunen, H.L.: Low temperature co-fired ceramics with ultra-low sintering temperature: A review, Curr. Opin. Solid. St. M., **20**, 151 – 170, (2016).

9 Zhou, D., Randall, C.A., Pang, L.X., Wang, H., Guo, J., Zhang, G.Q., Wu, X.G., Shui, L., Yao, X.: Microwave dielectric properties of Li_2WO_4 ceramic with ultra-low sintering temperature, J. Am. Ceram. Soc., **94**, 348 – 350, (2011).

10 Li, J., Fang, L., Luo, H., Khaliq, J.B., Tang, Y., Li, C.C.: Li_4WO_5: A temperature stable low-firing microwave dielectric ceramic with rock salt structure, J. Eur. Ceram. Soc., **36**, 243 – 246, (2016).

11 Zhou, H.F., Chen, X.L., Fang, L., Liu, X.B., Wang, Y.L.: Microwave dielectric properties of $LiBiW_2O_8$ ceramics with low sintering temperature, J. Am. Ceram. Soc., **93**, 3976 – 3979, (2010).

12 Fang, L., Wei, Z.H., Guo, H.H., Sun, Y.H., Tang,Y., Li, C.C.: Phase composition and microwave dielectric properties of low-firing $Li_2A_2W_3O_{12}$ (A = Mg, Zn) ceramics, J. Mater. Sci.-Mater. El., **26**, 5892 – 5895, (2015).

13 Shannon, R.D., Rossman, G.R.: Dielectric constants of silicate garnets and the oxide additivity rule, Am. Mineral, **77**, 94 – 100, (1992).

14 Cai, H., Li, L., Sun, H., Gao, Z., and Lu, X.: A temperature stable microwave dielectric material $Ni_{0.35}Zn_{0.65}TiNb_2O_8$, J. Matter. Sci. Mater. El., 26, 998 – 1003, (2015).

15 Liu, C., Zhang, H., Wang, G., Zhou, T., Su, H., Jia, L.: Novel thermal-stable low temperature sintered $Ba_2LiMg_2V_3O_{12}$ microwave dielectric ceramics with ZnO-P_2O_5-MnO_2 glass addition, Mater. Res. Bull., 93, 16 – 20, (2017).

16 Petzelt, J., Pacesova, S., Fousek, J., Kamba, S., Zelezny, V., Koukal, C.: Dielectric spectra of some ceramics for microwave applications in the range of 1010 – 1014 Hz, Ferroelectrics, **93**, 77 – 85, (1989).

17 Zhou, H.F., Gong, J.Z., Xu, J., Fan, G.C.: Novel 5MgO-3Li_2O-4WO_3 ceramic: preparation, phase evolution and its microwave dielectric properties, J. Mater. Sci-Mater. El., **27**, 6389 – 6394, (2016).

18 Zhou, H.F., Huang, J., Tan, X.H., Wang, N., Fan, G.C., Chen, X.L.: Compatibility with silver electrode and microwave dielectric properties of low firing $CaWO_4$ -2Li_2WO_4 ceramics, Mater. Res. Bull., **89**, 150 – 153, (2017).

19 Xie, H.D., Xi, H.H., Chen, C., Zhou, D.: Microwave dielectric properties of two low temperature sintering ceramics in the PbO - WO_3 binary system, Ceram. Int., **41**, 10287 – 10292, (2015).

20 Zhou, D., Pang, L.X., Xie, H.D., Guo, J., He, B., Qi, Z.M., Shao, T., Yao, X.,. Randall, C.A.: Crystal structure and microwave dielectric properties of an ultralow-temperature-fired $(Ag, Bi)_{0.5}WO_4$ ceramic, Eur. J. Inorg. Chem., **2014**, 296 – 301, (2014).