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Short communication

Low-firing and microwave dielectric properties of $Na_2YMg_2V_3O_{12}$ ceramic

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Abstract

A low-firing microwave dielectric ceramic $Na_2YMg_2V_3O_{12}$ with garnet structure was prepared via the conventional solid-state reaction method. X-ray diffraction data shows that $Na_2YMg_2V_3O_{12}$ ceramic crystallized into a cubic garnet structure with a space group *Ia-3d*. Dense $Na_2YMg_2V_3O_{12}$ ceramic with a relative density of 95.4% could be obtained when sintered at 850 °C and exhibited the optimum microwave properties with a relative permittivity of 12.3, a quality factor of 23,180 GHz (at 10.2 GHz), and a nearly zero τ_f value of −4.1 ppm/°C. $Na_2YMg_2V_3O_{12}$ was found to be chemically compatible with silver electrode when sintered at 850 °C. These merits make $Na_2YMg_2V_3O_{12}$ a good microwave dielectric ceramic with potential applications in LTCC technology.

Keywords: Microwave dielectric ceramics; Garnet structure; $Na_2YMg_2V_3O_{12}$; LTCC

1. Introduction

In recent years, low-temperature co-fired ceramics (LTCC) technology plays a key pole in the fabrication of miniature multilayer devices. The microwave dielectric materials used in the fabrication of LTCC devices have to be sintered below the melting points of the inner electrodes such as Ag electrode (961 °C) [1–4]. Meanwhile, the excellent substrate materials in microwave integrated circuits should also have a low dielectric constant (ε_r) to reduce the signal transmit delay, a high quality factor ($Q \times f$) for frequency selectivity, and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stability [5–7]. Up to now, numerous microwave ceramics that could be well densified at temperatures lower than 960 °C have been developed, such as V_2O_5–based [8,9], TeO_2–based [10,11], Bi_2O_3–based [12,13], Li_2O–based [14], WO_3–based [15] systems.

In our previous work, some garnet vanadates with a general formula $A_3B_2V_3O_{12}$ were investigated and reported with good microwave dielectric properties, such as $NaCa_2Mg_2V_3O_{12}$ (ε_r=10, $Q \times f$=50,600 GHz and τ_f=−47 ppm/°C) [16] and $LiCa_3MgV_3O_{12}$ (ε_r=10.5, $Q \times f$=74,700 GHz and τ_f=−61 ppm/°C) [17]. The combination merits of low sintering temperatures and promising microwave dielectric properties opens up their possible applications in LTCC technology. Yao *et al.* [18,19] firstly reported the microwave dielectric properties of some $Ca_5A_4(VO_4)_6$ (A=Mg, Zn, and Co) garnets with high quality factors (49,400–95,200 GHz), low relative permittivities (9.2–11.7), and large negative temperature coefficients of resonant frequency (−50 to −83 ppm/°C). However, the large negative τ_f values are problematic because temperature compensation needs additional mechanical structures or electrical circuits, which would impede their practical applications to a large extent. In our previous work, near-zero τ_f garnets were achieved by compensating the large negative τ_f with $CaTiO_3$ having a positive one (~ +800 ppm/°C). This

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approach, in spite of the effective adjustment of τ_f values, could cause an abrupt degradation of the quality factor. If different thermal expansion (different compositions), different thermal conductivity, and increasing reaction possibility with the inner electrode are taken into account, this method is not desirable. Thus, searching for microwave ceramics with intrinsic low thermal coefficient of resonance frequency is extremely important.

More recently, Zhou *et al.* [20] developed a temperature stable garnet vanadate $Na_2BiMg_2V_3O_{12}$ with a near-zero $\tau_f \sim +8.2$ ppm/°C, a $\varepsilon_r \sim 23.2$ and a $Q \times f \sim$ 3700 GHz. Therefore, it is worthwhile to investigate the $Na_2M^{3+}Mg_2V_3O_{12}$ system with an attempt to search for novel temperature stable microwave dielectric ceramics. In the present work, a garnet vanadate $Na_2YMg_2V_3O_{12}$ ceramic was prepared and its sintering behavior, microwave dielectric properties, and the chemical compatibility with silver electrodes were studied.

2. Experimental procedure

$Na_2YMg_2V_3O_{12}$ ceramic was prepared by a conventional solid-state reaction of Na_2CO_3 (99%, Guo-Yao Co. Ltd., Shanghai, China), Y_2O_3 (99.99%, Guo-Yao Co. Ltd., Shanghai, China), MgO (99%, Guo-Yao Co. Ltd., Shanghai, China) and NH_4VO_3 (> 99%, West Long Chemical Co., Ltd., Guangdong, China). Prior to weighting, MgO was heated at 900 °C for 2 h to remove moisture. Stoichiometric powers were weighted and mixed by ball milling for 4 h in alcohol medium using stabilized zirconia balls. The power mixture was dried and calcined at 760 °C for 4 h in air. The calcined powders were re-milled for 4 h and after drying, the polyvinyl alcohol (PVA, 10 vol%) was added to the powders as binder. Then the powders were pressed into cylinders (12 mm in diameter and 7 mm in height) under a pressure of 200 MPa. The samples were heated to 550 °C for 2 h at a heating rate of 1.5 °C/min to remove the organic binder and sintered from 780 °C to 880 °C for 4 h in air.

The crystal structure of the specimens was identified using an X-ray diffractometer (Cu*Kα1*, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland) with Cu*Kα* radiation and a monochromator. The bulk densitie of the sintered ceramics were determined by the Archimedes method. The surface micrographs of the samples were observed by scanning electron microscope (FE-SEM, Model S4800, Hitachi, Japan). The microwave dielectric properties were measured using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range from 25 °C–85 °C.

3. Results and discussion

Fig.1 shows the XRD pattern of $Na_2YMg_2V_3O_{12}$ powders calcined at 760 °C for 4 h. The observed peaks matched well with the standard JCPDS Card no. 00-049-0412, and no additional peaks were observed. The indexing was based on

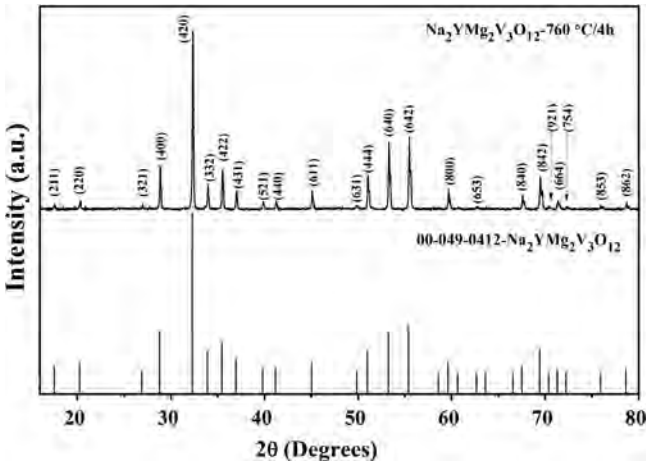

Fig. 1. The powder XRD pattern of $Na_2YMg_2V_3O_{12}$ calcined at 760 °C for 4 h.

the standard JCPDS card. This result means that single-phase $Na_2YMg_2V_3O_{12}$ with a cubic garnet structure with space group of *Ia-3d* (230) could be formed at 760 °C.

Fig.2 shows the SEM micrographs and the relative densities of $Na_2YMg_2V_3O_{12}$ ceramic sintered at different temperatures. As shown in Fig.2(a), a porous microstructure with small grains ~3 μm was observed in the ceramic sintered at 780 °C. With the increasing sintering temperature, the grain size increased along with a significant decrease in the porosity. The sample sintered at 850 °C exhibited a well dense microstructure with average grain size in the range of 3–5 μm. When the sintering temperature increased to 880 °C, the grain melting was observed. Fig.2(f) shows the relative density of $Na_2YMg_2V_3O_{12}$ ceramics sintered at different temperatures. With the increase in sintering temperature, the relative density of $Na_2YMg_2V_3O_{12}$ ceramic increased initially, reached a maximum value ~3.51 g/cm^3 (about 95.4% of the theoretical density ~3.68 g/cm^3) at 880 °C, then slightly decreased with further increasing sintering temperature.

The variation in the microwave dielectric properties (ε_r, $Q \times f$, and τ_f) of $Na_2YMg_2V_3O_{12}$ ceramics as a function of the sintering temperature are shown in Fig.3. The change in the relative permittivity and quality factor showed a similar trend as that of the relative density. ε_r increased from 11.8 to 12.3 as the sintering temperature increased from 780 °C to 850 °C, and then slightly decreased. It is reported that the relative permittivity mainly depends on the composition, grain size and the density [21]. The largest ε_r value was obtained at which temperature the highest density was achieved. The influence of the porosity on the microwave permittivity could be eliminated by applying Bosman and Havinga's correction [22,23] as shown in Eq. (1)

$$\varepsilon_{corrected} = \varepsilon_m(1+1.5p) \quad (1)$$

where, p is the fractional porosity; $\varepsilon_{corrected}$ and ε_m are the corrected and measured values of permittivity, respectively. The $\varepsilon_{corrected}$ is about 13.15 for $Na_2YMg_2V_3O_{12}$ ceramic. Furthermore, ε_r can be interpreted by the sum of ionic polarizability of individual ions (α_D^T) and molar volume (V_m)

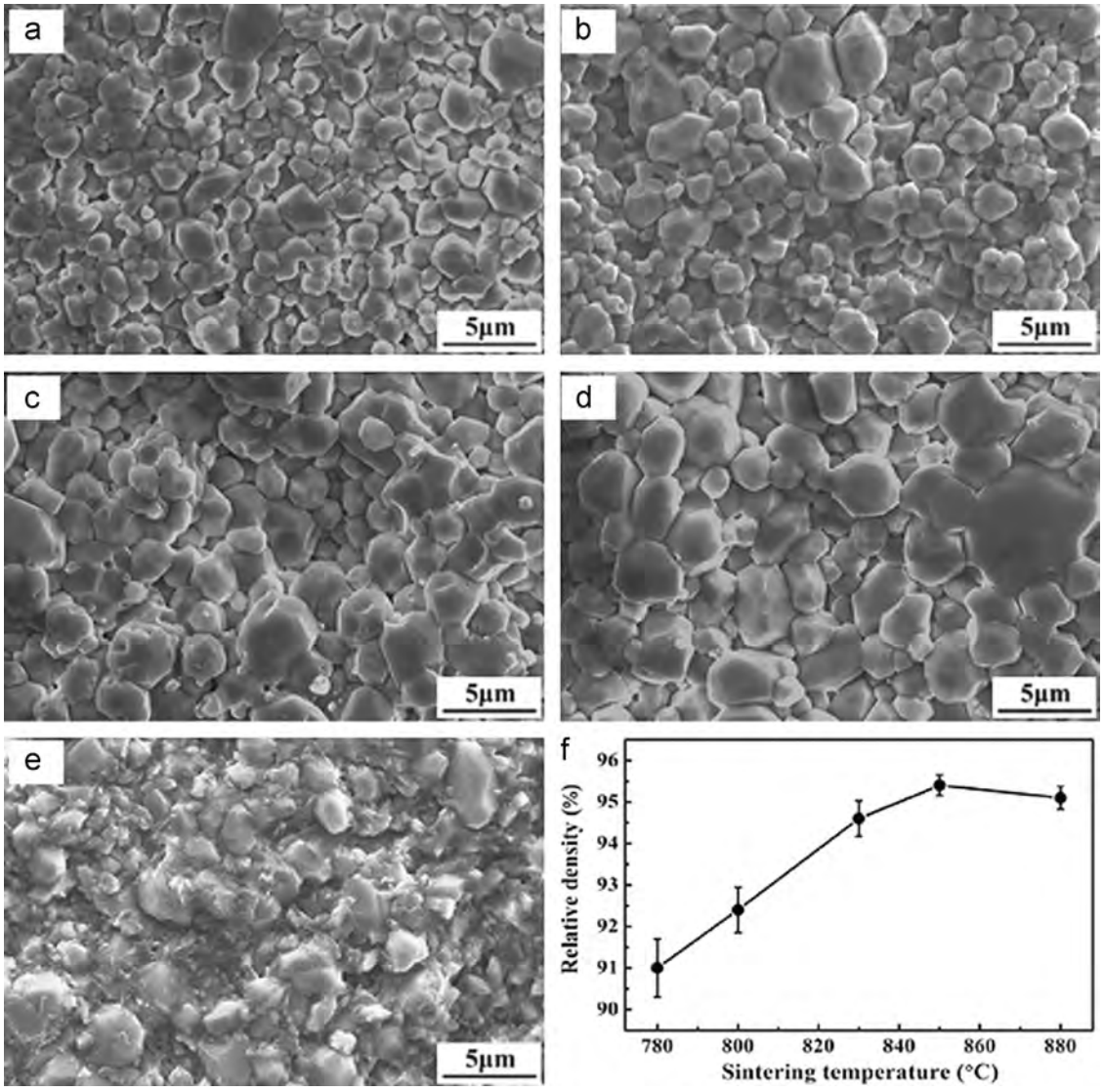

Fig. 2. SEM micrographs and the relative density of $Na_2YMg_2V_3O_{12}$ ceramic sintered at different temperatures: (a) 780 °C, (b) 800 °C, (c) 830 °C, (d) 850 °C, (e) 880 °C, and (f) the relative density.

according to Clausius–Mossotti equation [24,25]:

$$\varepsilon_r = \frac{1+2b\alpha_D^T/V_m}{1-b\alpha_D^T/V_m} \quad (2)$$

where, $b=4\pi/3$. The calculated theoretical permittivity of $Na_2YMg_2V_3O_{12}$ is 11.6. The relative error of $Na_2YMg_2V_3O_{12}$ is about 6.0% for the measured value and 13.3% for the porosity corrected value, which means that there is another polarization mechanism in the $Na_2YMg_2V_3O_{12}$ ceramic at microwave region beside ionic and electronic displacement polarization [26].

As the sintering temperature increased, the $Q\times f$ value of $Na_2YMg_2V_3O_{12}$ ceramic increased and then reached a maximum value of ~23,180 GHz sintered at 850 °C. Thereafter, the $Q\times f$ value decreased with further increase in sintering temperature. In general, the factors affecting the dielectric loss at microwave region can be classified into two categories: the intrinsic losses and the extrinsic ones [27]. Usually, the extrinsic dielectric losses caused by the universal defects (impurities, substitution, grain boundaries, grain morphology and shape, secondary phase, pores, etc.) dominate the $Q\times f$ value in ceramics. Until now, it is still difficult to accurately calculate the extrinsic losses in polycrystalline samples [28]. The τ_f values of $Na_2YMg_2V_3O_{12}$ ceramic varied in the range from −6.1 to −4.1 ppm/°C over the sintering region from 780 °C to 850 °C. A near-zero τ_f value of −4.1 ppm/°C was achieved for sample sintered at 850 °C.

Table 1 lists the sintering temperatures and the microwave dielectric properties of a series of garnet vanadates. As shown, all the ceramics have low relative permittivity between 10 and 13. The sintering temperature (~850 °C) of $Na_2YMg_2V_3O_{12}$ ceramic is competitive to the other garnets. It is worth noting that the temperature coefficient of resonance frequency of $Na_2YMg_2V_3O_{12}$ is near-zero with a value ~−4.1 ppm/°C. The temperature stability, low relative permittivity and relatively high quality factor along with the low sintering temperature make $Na_2YMg_2V_3O_{12}$ a possible candidate in LTCC applications.

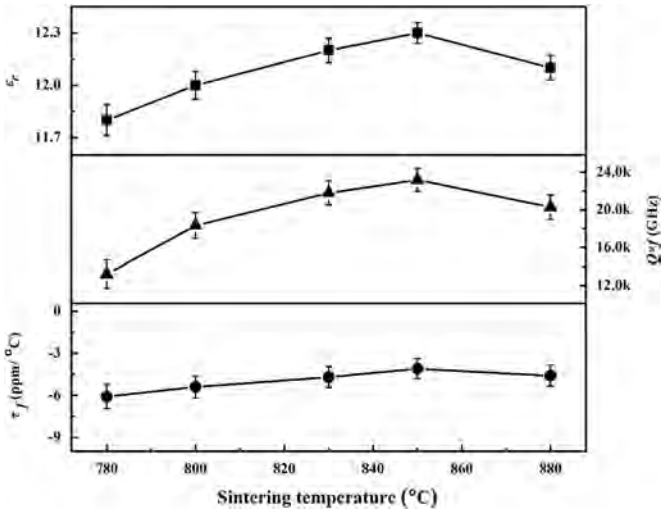

Fig. 3. ε_r, $Q\times f$, and τ_f values of $Na_2YMg_2V_3O_{12}$ ceramics sintered at different temperatures from 780 to 880 °C.

Table 1
Comparison of microwave dielectric properties of some garnet vanadates ceramics

Composition	S.T. (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	Reference
$NaCa_2Mg_2V_3O_{12}$	915	10	50,600	−47	[16]
$LiCa_3MgV_3O_{12}$	900	10.5	74,700	−61	[17]
$Ca_5Co_4(VO_4)_6$	875	10.6	95,200	−63	[19]
$LiCa_3ZnV_3O_{12}$	900	11.5	81,100	−72	[29]
$Ca_5Zn_4(VO_4)_6$	725	11.7	49,400	−83	[18]
$Na_2YMg_2V_3O_{12}$	850	12.3	23,180	−4.1	This work

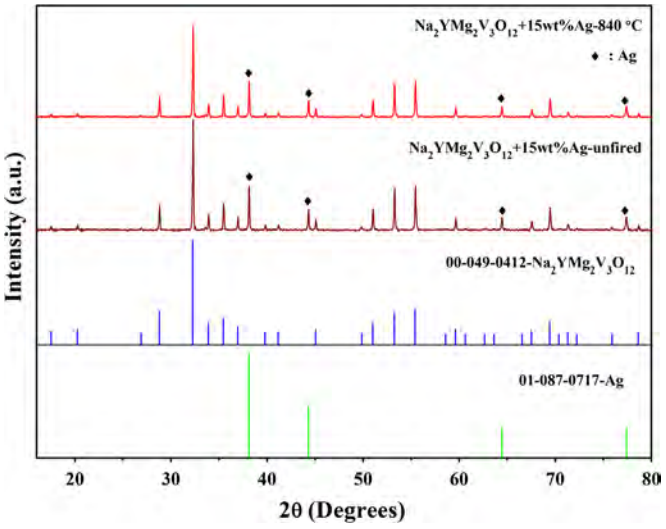

Fig. 4. XRD patterns of unfired $Na_2YMg_2V_3O_{12}$ with 15 wt% silver and the cofired sample at 840 °C.

For chemical compatibility experiment, 15 wt% Ag powders was mixed with $Na_2YMg_2V_3O_{12}$ ceramic and fired at 850 °C to detect the interaction between the sample and electrode. XRD patterns of the unfired mixture of $Na_2YMg_2V_3O_{12}$ and 15 wt% Ag powders and the cofired sample are shown in Fig. 4. From XRD patterns, only the peaks belonging to $Na_2YMg_2V_3O_{12}$ and Ag could be observed without secondary phase detected. In addition, by comparison of the XRD patterns before and after co-firing, it is noted that the relative intensities of the peaks are almost the same. These results suggest no reaction between $Na_2YMg_2V_3O_{12}$ and Ag. This was further confirmed from the backscattered electron image and EDS analysis, as shown in Fig. 5. Two distinct grains could be seen and the larger bright grains were detected to be Ag.

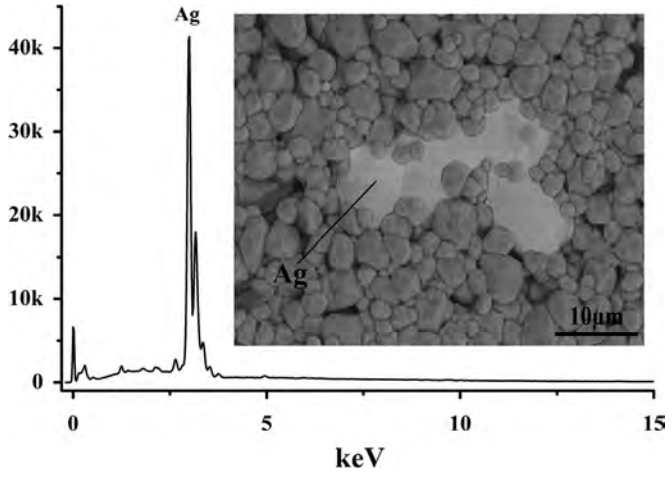

Fig. 5. Backscattered electron image micrograph and EDS analysis of the $Na_2YMg_2V_3O_{12}$ ceramic with 15 wt% silver powder fired at 840 °C.

4. Conclusions

In summary, a cubic garnet structured $Na_2YMg_2V_3O_{12}$ ceramic was prepared by the conventional solid-state reaction method. Dense $Na_2YMg_2V_3O_{12}$ ceramic with a relative density of 95.4% could be obtained when sintered at 850 °C. $Sr_2NaMg_2V_3O_{12}$ ceramic sintered at 850 °C for 4 h, with a permittivity of 12.3, $Q\times f$ value of 23,180 GHz, and a nearly zero τ_f value of −4.1 ppm/°C. $Na_2YMg_2V_3O_{12}$ was found to be chemically compatible with silver electrode when sintered at 850 °C. All the results indicate that the $Na_2YMg_2V_3O_{12}$ ceramic is a potential candidate for low-temperature co-fired ceramics technology.

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References

[1] Y. Higuchi, Y. Sugimoto, J. Harada, H. Tamura, LTCC system with new high-ε_r and high-Q material Co-fired with conventional low-ε_r base

material for wireless communications, J. Eur. Ceram. Soc. 27 (2007) 2785–2788.
[2] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, Int. Mater. Rev. 53 (2008) 57–90.
[3] D. Zhou, L.X. Pang, H. Wang, X. Yao, Low temperature firing microwave dielectric ceramics ($K_{0.5}Ln_{0.5}$)MoO_4 (Ln=Nd and Sm) with low dielectric loss, J. Eur. Soc. 31 (2011) 2749–2752.
[4] D. Zhou, L.X. Pang, J. Guo, Z.M. Qi, T. Shao, Q.P. Wang, H.D. Xie, X. Yao, C.A. Randall, Influence of Ce substitution for Bi in $BiVO_4$ and the impact on the phase evolution and microwave dielectric properties, Inorg. Chem. 53 (2014) 1048–1055.
[5] Q.W. Liao, L.X. Li, X. Ren, X. Ding, New low-loss microwave dielectric material $ZnTiNbTaO_8$, J. Am. Ceram. Soc. 94 (2011) 3237–3240.
[6] I.M. Reaney, D. Iddles, Mcrowave dielectric ceramics for resonators and filters in mobile phone networks, J. Am. Ceram. Soc. 89 (2006) 2063–2072.
[7] J. Li, C.C. Li, Z.H. Wei, Y. Tang, C.X. Su, L. Fang, Microwave dielectric properties of a low-firing $Ba_2BiV_3O_{11}$ ceramic, J. Am. Ceram. Soc. 98 (2015) 683–686.
[8] R. Umemura, H. Ogawa, H. Ohsato, A. Kana, A. Yokoi, Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2$ ceramic, J. Eur. Ceram. Soc. 25 (2005) 2865–2870.
[9] L. Fang, Z.H. Wei, C.X. Su, F. Xiang, H. Zhang, Novel low-firing microwave dielectric ceramics: $BaMV_2O_7$ (M=Mg, Zn), Ceram. Int. 40 (2014) 16835–16839.
[10] D.K. Kwon, M.T. Lanagan, T.R. Shrout, Microwave Dielectric properties and low-temperature cofiring of $BaTe_4O_9$ with aluminum metal electrode, J. Am. Ceram. Soc. 88 (2005) 3419–3422.
[11] G. Subodh, M.T. Sebastian, Glass-free $Zn_2Te_3O_8$ microwave ceramic for LTCC applications, J. Am. Ceram. Soc. 90 (2007) 2266–2268.
[12] M. Valant, D. Suvorov, Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20}$-delta (M=Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$), J. Am. Ceram. Soc. 84 (2001) 2900–2904.
[13] D. Zhou, H. Wang, L.X. Pang, C.A. Randall, X. Yao, Bi_2O_3–MoO_3 binary system: an alternative ultra low sintering temperature microwave dielectric, J. Am. Ceram. Soc. 92 (2009) 2242–2246.
[14] M. Valant, D. Suvorov, Chemical compatibility between silver electrodes and low-firing binary-oxide compounds: conceptual study, J. Am. Ceram. Soc. 83 (2000) 2721–2729.
[15] T. Takada, S.F. Wang, S. Yoshikawa, S.J. Jang, R.E. Newnham, Effect of glassadditions on BaO–TiO_2–WO_3 microwave ceramics, J Am Ceram Soc. 77 (1994) 1909–1916.
[16] L. Fang, F. Xiang, C.X. Su, H. Zhang, A novel low firing microwave dielectric ceramic $NaCa_2Mg_2V_3O_{12}$, Ceram. Int. 39 (2013) 9779–9783.
[17] L. Fang, C.X. Su, H.F. Zhou, Z.H. Wei, H. Zhang, Novel low-firing microwave dielectric ceramic $LiCa_3MgV_3O_{12}$ with low dielectric loss, J. Am. Ceram. Soc. 96 (2013) 688–690.
[18] G.G. Yao, P. Liu, X.G. Zhao, J.P. Zhou, H.W. Zhang, Low-temperature sintering and microwave dielectric properties of $Ca_5Co_4(VO_4)_6$ ceramics, J. Eur. Ceram. Soc. 34 (2014) 2983–2987.
[19] G.G. Yao, P. Liu, H.W. Zhang, Novel series of low-firing microwave dielectric ceramics: $Ca_5A_4(VO_4)_6$ (A^{+2}=Mg, Zn), J. Am. Ceram. Soc. 96 (2013) 1691–1693.
[20] H.F. Zhou, Y.B. Miao, J. Chen, X.L. Chen, F. He, D.D. Ma, Sintering characteristic, crystal structure and microwave dielectric properties of a novel thermally stable ultra-low-firing $Na_2BiMg_2V_3O_{12}$ ceramic, J. Mater. Sci. Mater. Electron. 25 (2014) 2470–2474.
[21] S. George, P.S. Anjana, V. Deepu, P. Mohanan, M.T. Sebastian, Low-temperature sintering and microwave dielectric properties of Li_2MgSiO_4 ceramics, J. Am. Ceram. Soc. 92 (2009) 1244–1249.
[22] A.J. Bosman, E.E. Havinga, Temperature dependence of dielectric constants of cubic ionic compounds, Phys. Rev. 129 (1963) 1593–1600.
[23] D.W. Kim, I.T. Kim, B. Park, K.S. Hong, J.H. Kim, Microwave dielectric properties of $(1-x)Cu_3Nb_2O_{8-x}Zn_3Nb_2O_8$ ceramics, J. Mater. Res. 16 (2001) 1465–1470.
[24] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.
[25] S.H. Yoon, D.W. Kim, S.Y. Cho, H.K. Sun, Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds, J. Eur. Ceram. Soc. 26 (2006) 2051–2054.
[26] D. Zhou, H. Wang, X. Yao, L.X. Pang, Microwave dielectric properties of low temperature firing $Bi_2Mo_2O_9$ ceramic, J. Am. Ceram. Soc. 91 (2008) 3419–3422.
[27] C.F. Tseng, Microwave dielectric properties of a new $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics, J. Eur. Ceram. Soc. 35 (2015) 383–387.
[28] D. Zhou, C.A. Randall, H. Wang, X. Yao, Microwave dielectric properties of Li_2WO_4 ceramic with ultra-low sintering temperature, J. Am. Ceram. Soc. 94 (2011) 348–350.
[29] C.X. Su, L. Fang, Z.H. Wei, X.J. Kuang, H. Zhang, $LiCa_3ZnV_3O_{12}$: a novel low-firing, high Q microwave dielectric ceramic, Ceram. Int. 40 (2014) 5015–5018.