Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 3737–3741

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

$Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ solid solution: Microstructural evolution, optimized sintering behavior and microwave dielectric properties

Huanfu Zhou*, Xiuli Chen, Liang Fang, Wei Wang

Guangxi Scientific Experiment Center of Mining, Metallurgy and Environment, Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China

Received 19 August 2013; received in revised form 10 September 2013; accepted 11 September 2013
Available online 29 September 2013

Abstract

Microwave dielectric ceramics with the composition of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ (CZNV, $0 \leq x \leq 0.02$) were prepared by the solid-state reaction method. The sintering behavior, phase structure, and microwave dielectric properties of CZNV ceramics were investigated. All samples sintered at 1125–1225 °C for 3 h remained a single phase. However, the grain shape changed from equiaixed to rectangle with increasing x. The dielectric properties of CZNV solid solution exhibited a significant dependence on the sintering condition, microstructure and composition. The $Q \times f$ value and temperature coefficient of resonant frequency (τ_f) can be improved with substituting V for Nb. As $x=0.005$, $Ca(Zn_{0.333}Nb_{0.662}V_{0.005})O_3$ ceramic sintered at 1200 °C for 3 h in air exhibited good microwave dielectric properties with $\varepsilon_r=34.3$, $Q \times f=16{,}420$ GHz, and $\tau_f=-17.6$ ppm/°C.

Keywords: A. Sintering; B. X-ray methods; C. Dielectric properties; D. Perovskites; E. Functional applications

1. Introduction

Microwave dielectric ceramics have been widely utilized for filters and stabilizers of the frequency oscillation in microwave integrated circuits. The materials used in these microwave devices are required to have a high relative permittivity (ε_r), high quality factor (Q), and small temperature coefficient of the resonant frequency (τ_f) [1–3]. Complex perovskite compounds, such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, and $Ba(Zn_{1/3}Nb_{2/3})O_3$, are well-known as high-Q microwave dielectric ceramics, and they have important applications as resonators and filters in microwave communication systems [4–10]. As one kind of complex perovskite materials, calcium-based complex perovskite ceramics have also been recognized as the low-loss dielectrics. Among calcium-based complex perovskite compounds, $Ca(Mg_{1/3}Ta_{2/3})O_3$ and $Ca(Mg_{1/3}Nb_{2/3})O_3$ have received much attention because of their very high $Q \times f$ values (78,000 GHz for the former and 58,000 GHz for the latter) [11]. The modification of $Ca(Mg_{1/3}Nb_{2/3})O_3$ and $Ca(Mg_{1/3}Ta_{2/3})O_3$ ceramics by incorporating $CaTiO_3$ has been reported to achieve near-zero temperature coefficient of resonant frequency [12–15].

Kagata et al. [11] first reported that $Ca(Zn_{1/3}Nb_{2/3})O_3$ possessed a good microwave dielectric property with $\varepsilon_r=35$, $Q \times f = 16{,}000$ GHz, and $\tau_f=-48$ ppm/°C. After that, Chen et al. [16] studied the process and microstructure dependence of the microwave dielectric characteristics of $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic. They found that the microwave dielectric properties of $Ca(Zn_{1/3}Nb_{2/3})O_3$ were greatly influenced by the sintering process, the $Ca(Zn_{1/3}Nb_{2/3})O_3$ sintered at 1225 °C for 3 h in air and annealed at 1100 °C in oxygen for 8 h exhibited a similar Q value to Kagata's work. Liu et al. [17] obtained a near-zero τ_f $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic by adding $CaTiO_3$.

Zhou et al. reported that V substitution can improve the microwave dielectric properties of some ceramics with high quality values, such as $xBi(Fe_{1/3}Mo_{2/3})O_4-(1-x)BiVO_4$ [18], $(A_{0.5x}Bi_{1-0.5x})(Mo_xV_{1-x})O_4$ (A=Li, Na) [19–21], $Bi(V_xNb_{1-x})O_4$ [22]. In the present work, V was used as a substitute for Nb to optimize the sintering process and increase

*Corresponding author. Tel.: +86 773 5893395; fax: +86 773 5896436.
E-mail address: zhouhuanfu@163.com (H. Zhou).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.09.048

the Q value of the $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic. Furthermore, the sintering behavior, phase structure and microwave dielectric properties of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics were investigated.

2. Experimental procedure

$Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ (x=0.002, 0.005, 0.01, 0.02) ceramics were prepared by a conventional solid-state reaction method from the high-purity raw powders of $CaCO_3$ (≥ 99%), ZnO (≥ 99%), V_2O_5 (≥ 99.9%) and Nb_2O_5 (≥ 99%). Stoichiometric proportions of CZNV were mixed in alcohol medium using zirconia balls for 4 h and calcined at 1150 °C for 3 h in air. The calcined powders were milled again with ZrO_2 balls for 4 h in alcohol medium. After drying, a 5 wt% poly (vinyl alcohol) (PVA) solution was added to the powders and the resulting mixture was pressed into disks of 12 mm in diameter and ~6 mm in thickness at a uniaxial pressure of about 200 MPa. The samples were then heat-treated at 550 °C for 4 h to eliminate PVA, followed by sintering at 1125–1225 °C for 3 h in air at a heating rate of 5 °C/min.

The bulk density of the sintered samples was measured by Archimedes method. The crystal structure of samples was investigated by X-ray diffractometer (XRD) (CuKα1, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland). The surface micrographs of the samples were examined using a scanning electron microscope (SEM, Model JSM6380-LV, JEOL, Tokyo, Japan). Microwave dielectric properties were measured by the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (Model N5230A, Agilent Co., Palo Alto, CA) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA).

The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T, f_0 are the resonant frequencies at the measuring temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of CZNV ceramics sintered at 1200 °C for 3 h. The crystal structure of $Ca(Zn_{1/3}Nb_{2/3})O_3$ was known as the complex perovskite structure. When V was used as a substitute for Nb, the sintered CZNV ceramics also exhibited a complex perovskite structure. The indexed XRD patterns did not reveal a secondary phase structure for all compositions. Fig. 2 shows the relative density of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics sintered at different temperatures. The densified temperatures are the temperatures which could achieve the highest relative density for each composition. It was found that the relative densities have the maximum values at around 1200 °C. Either higher or lower sintering temperatures may cause the relative density to decrease, especially when the sintering temperature is below 1150 or above 1200 °C.

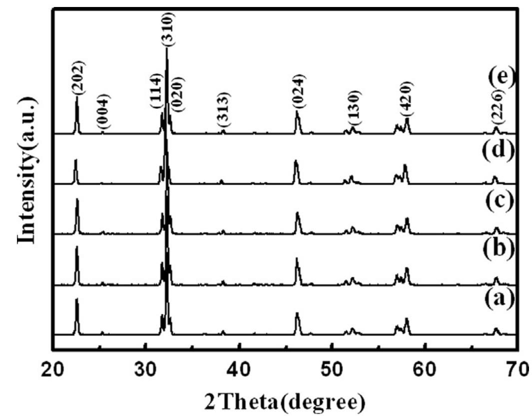

Fig. 1. XRD patterns of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics sintered at 1200 °C for 3 h: (a) x=0, (b) x=0.002, (c) x=0.005, (d) x=0.01, and (e) x=0.02.

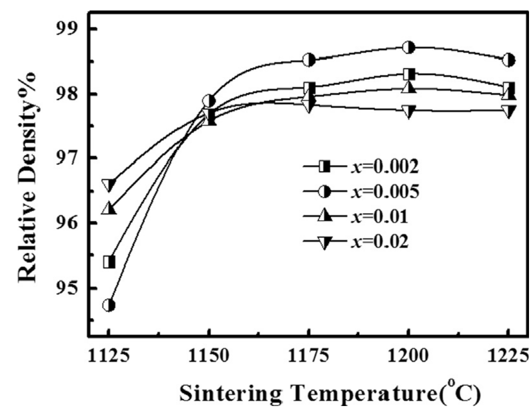

Fig. 2. Relative density of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of sintering temperature.

SEM pictures of the $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics sintered at 1200 °C for 3 h are illustrated in Fig. 3. When $x \leq 0.005$, the grain sizes were uniform, and no pores were observed (Fig. 3(a) and (b)). However, when x was over 0.005, there were many plate-like crystallites, as seen in Fig. 3(c). The size of the plate-like crystallites was about 5 μm. And when x was 0.02, the size of plate-like crystallites became much bigger. XRD revealed that there is no difference between the surface and powder of samples. So EDS analysis was performed to identify the compositional difference between two types of grains, as shown in Fig. 4. The results show that there were no various compositional differences between large and small grains. The grain shape of samples changed from equiaxed to plate-like as x varied from 0002 to 0.02 (Fig. 3(a–d)). This phenomenon might be related to the oriented growth of grains caused by the formation of solid solution.

Fig. 5 shows the curves of the relative permittivity of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of the sintering temperature. The relationship between ε_r value and sintering temperature presents a trend similar to that of density and sintering temperature. The specimens exhibited maximum ε_r at 1150–1200 °C, which agrees well with the analysis of densities (Fig. 1). Comparing with Nb, V has a lower ionic polarizability. So the relative permittivity (ε_r) decreased with increasing the

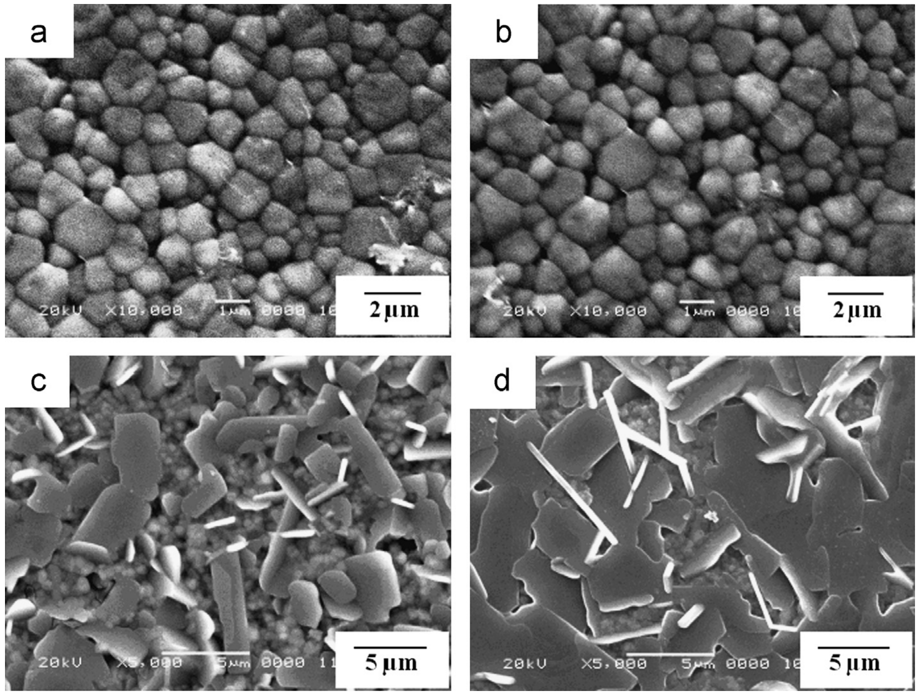

Fig. 3. SEM images of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics sintered at 1200 °C for 3 h: (a) $x=0.002$, (b) $x=0.005$, (c) $x=0.01$, and (d) $x=0.02$.

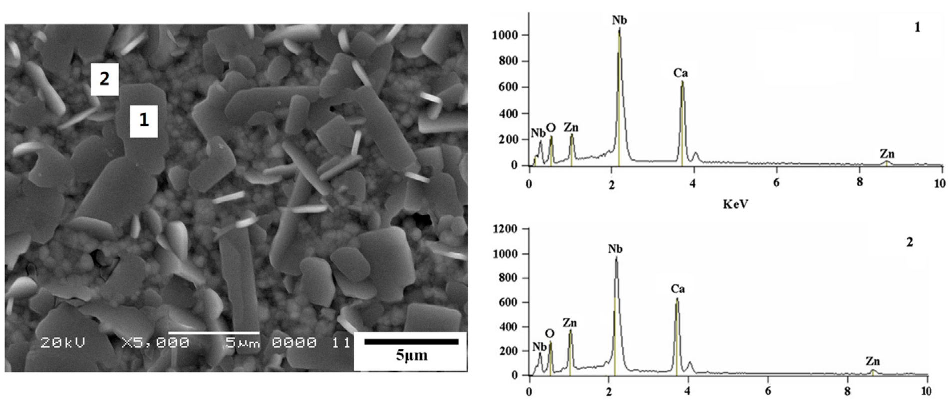

Fig. 4. EDS spectra obtained from $Ca(Zn_{0.333}Nb_{0.657}V_{0.01})O_3$ ceramic.

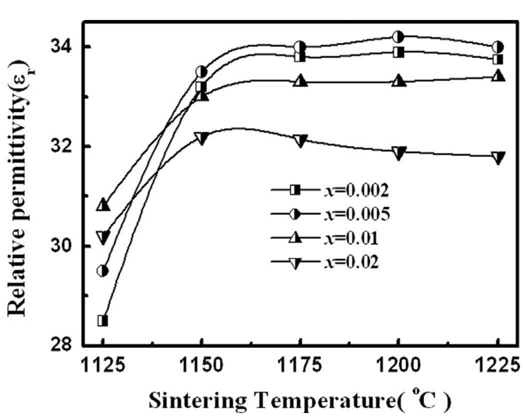

Fig. 5. Relative permittivity (ε_r) of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of sintering temperature.

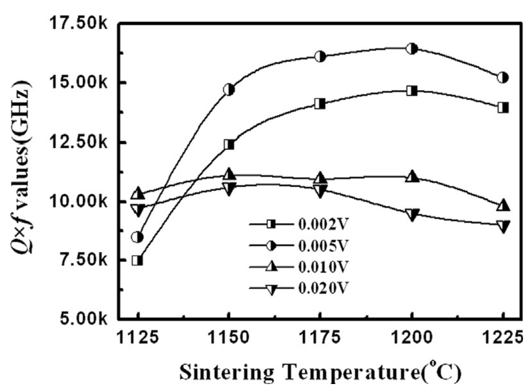

Fig. 6. $Q\times f$ value of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of sintering temperature.

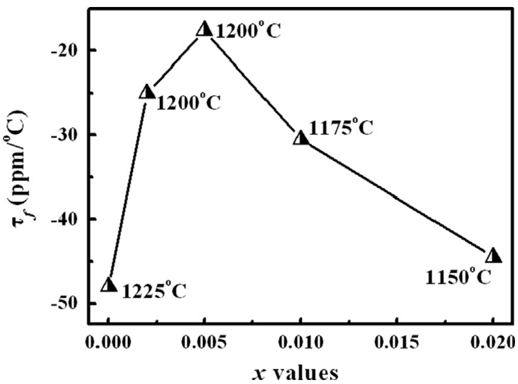

Fig. 7. Temperature coefficient of the resonant frequency τ_f of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of x.

substitution of V. Fig. 6 shows the $Q\times f$ value of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics as a function of the sintering temperature. The measured Q factors were obtained at different resonant frequencies depending on the physical dimensions and relative permittivity. According to the generally observed relationship, $Q\times f=$constant, where f is the resonant frequency and Q is the value calculated from the $TE_{01\delta}$ resonator method. Generally, microwave dielectric loss includes two parts, including intrinsic loss and extrinsic loss. Intrinsic losses were caused by absorptions of phonon oscillation and extrinsic losses were caused by lattice defects. The lattice defects include impurity, cavity, substitution, size and shapes of grains, second phase, pores, etc. [23, 24] The relationship between the $Q\times f$ value of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics and sintering temperature also shows a trend similar to that of density and sintering temperature. Higher density indicates lower porosity, the $Q\times f$ values increased with increasing the sintering temperatures. After reaching a maximum value, the $Q\times f$ value decreased because of oversintering. Due to the changes of microstructure, the $Q\times f$ values of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics first increased, reached a maximum value, and decreased with increasing the substitution of V for Nb. The composition dependence of τ_f in $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics sintered at 1200 °C for 3 h were shown in Fig. 7. The intrinsic factor of microstructure variation and the extrinsic factor of phase assemblage were believed to determine the τ_f characteristic. It was observed that the τ_f value first increased and then decreased with increasing x. The τ_f value varied from -48 to -17.6×10^{-6}/°C as x increased from 0 to 0.02.

In a previous work [16], the sintering process, such as cooling rate, sintering atmosphere, etc. has a great effect on the microwave dielectric properties (especially for $Q\times f$ value) of the $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic. The $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic sintered at 1225 °C for 3 h in air and annealed at 1100 °C in oxygen for 8 h exhibited good properties with $\varepsilon_r=34.1$, $Q\times f=15{,}890$ GHz, and $\tau_f=-48$ ppm/°C. By contrast, small amount of V substitution for Nb can stabilize the sintering process and improve the $Q\times f$ value of $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramic. $Ca(Zn_{0.333}Nb_{0.662}V_{0.005})O_3$ ceramic sintered at 1200 °C for 3 h in air exhibited good microwave dielectric properties with $\varepsilon_r=34.3$, $Q\times f=16{,}420$ GHz, and $\tau_f=-17.6$ ppm/°C.

4. Conclusions

The sintering behavior, phase structure, and microwave dielectric properties of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ solid solution have been investigated. The dielectric properties of $Ca(Zn_{1/3}Nb_{2/3-x}V_x)O_3$ ceramics exhibited a significant dependence on the sintering condition, microstructure and compositions of ceramics. The relationship between microwave dielectric properties and process was interpreted through the variation of microstructures. The relative permittivity decreased, but the $Q\times f$ and τ_f values can be improved with substituting V for Nb. When $x=0.005$, the samples exhibited excellent microwave dielectric properties: $\varepsilon_r=34.3$, $Q\times f=16{,}420$ GHz, and $\tau_f=-17.6$ ppm/°C.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos. 51102058, 11364012, and 50962004), Project of Guangxi Scientific Research and Technical Development (No. 1348020-11), Natural Science Foundation of Guangxi (No. 2013GXNSFAA019291), Project of Guangxi Scientific Experiment Center of Mining, Metallurgy and Environment (No. KH2011YB019), Patent Project of Guangxi Department of Education (No. 2013ZL080), and Research Start-up Funds Doctor of Guilin University of Technology (Nos. 002401003281 and 002401003282).

References

[1] B. Fu, Y. Zhang, H. Yue, Microwave dielectric properties of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics, Ceramics International 39 (4) (2013) 3789–3793.

[2] X. Yao, H. Lin, X. Zhao, W. Chen, Effects of Al_2O_3 addition on the microstructure and microwave dielectric properties of $Ba_4Nd_{9.33}Ti_{18}O_{54}$ ceramics, Ceramics International 38 (8) (2012) 6723–6728.

[3] S. Yu, S. Zhang, B. Tang, X. Zhou, Y. Fang, Microwave dielectric properties of $BaO-2(1-x)ZnO-xNd_2O_3-4TiO_2$ ($x=0$–1.0) ceramics, Ceramics International 38 (1) (2012) 613–618.

[4] M. Bieringer, S.M. Moussa, L.D. Noailles, A. Burrows, C.J. Kiely, M.J. Rosseinsky, R.M. Ibberson, Cation ordering, domain growth, and zinc loss in the microwave dielectric oxide $Ba_3ZnTa_2O_{9-\delta}$, Chemistry of Materials 15 (2) (2003) 586–597.

[5] P.K. Davies, J.Z. Tong, T. Negas, Effect of ordering-induced domain boundaries on low-loss $Ba(Zn_{1/3}Ta_{2/3})O_3$–$BaZrO_3$ perovskite microwave dielectrics, Journal of the American Ceramic Society 80 (7) (1997) 1727–1740.

[6] J.I. Yang, S. Nahm, C.H. Choi, H.J. Lee, H.M. Park, Microstructure and microwave dielectric properties of Ba $(Zn_{1/3}Ta_{2/3})$ O_3 ceramics with ZrO_2 addition, Journal of the American Ceramic Society 85 (1) (2002) 165–168.

[7] K.P. Surendran, M.T. Sebastian, Low loss dielectrics in $Ba[(Mg_{1/3}Ta_{2/3})_{1-x}Ti_x]O_3$ and $Ba[(Mg_{1-x}Zn_x)_{1/3}Ta_{2/3}]O_3$ systems, Journal of Materials Research 20 (11) (2005) 2919–2926.

[8] K.P. Surendran, M.T. Sebastian, P. Mohanan, R.L. Moreira, A. Dias, Effect of nonstoichiometry on the structure and microwave dielectric properties of $Ba(Mg_{0.33}Ta_{0.67})O_3$, Chemistry of Materials 17 (1) (2005) 142–151.

[9] M.W. Lufaso, Crystal structures, modeling, and dielectric property relationships of 2:1 ordered $Ba_3MM'_2O_9$ (M = Mg, Ni, Zn; M' = Nb, Ta) perovskites, Chemistry of Materials 16 (11) (2004) 2148–2156.

[10] M.W. Lufaso, E. Hopkins, S.M. Bell, A. Llobet, Crystal chemistry and microwave dielectric properties of $Ba_3MNb_{2-x}Sb_xO_9$ (M = Mg, Ni, Zn), Chemistry of Materials 17 (16) (2005) 4250–4255.
[11] H. Kagata, J. Kato, Dielectric properties of Ca-based complex perovskite at microwave frequencies, Japanese Journal of Applied Physics 33 (9B) (1994) 5463–5465.
[12] C.L. Huang, R.Y. Yang, M.H. Weng, Dielectric properties of $CaTiO_3$–$Ca(Mg_{1/3}Nb_{2/3})O_3$ ceramic system at microwave frequency, Japanese Journal of Applied Physics 39 (12A) (2000) 6608–6611.
[13] C.L. Huang, H.L. Chen, C.C. Wu, Improved high Q value of $CaTiO_3$–$Ca(Mg_{1/3}Nb_{2/3})O_3$ solid solution with near zero temperature coefficient of resonant frequency, Materials Research Bulletin 36 (9) (2001) 1645–1652.
[14] M.S. Fu, X.Q. Liu, X.M. Chen, Y.W. Zeng, Microstructure and microwave dielectric properties of $(1-x)Ca(Mg_{1/3}Ta_{2/3})O_3/xCaTiO_3$ ceramics, Journal of the American Ceramic Society 91 (4) (2008) 1163–1168.
[15] F. Zhao, Z. Yue, Y. Zhang, Z. Gui, L. Li, Microstructure and microwave dielectric properties of $Ca[Ti_{1-}x(Mg_{1/3}Nb_{2/3})x]O_3$ ceramics, Journal of the European Ceramic Society 25 (14) (2005) 3347–3352.
[16] X.M. Chen, D. Liu, R.Z. Hou, X. Hu, X.Q. Liu, Microstructures and microwave dielectric characteristics of $Ca(Zn_{1/3}Nb_{2/3})O_3$ complex perovskite ceramics, Journal of the American Ceramic Society 87 (12) (2004) 2208–2212.
[17] H. Liu, H. Yu, Z. Tian, Z. Meng, S. Ouyang, Dielectric properties of $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ ceramic system at microwave frequency, Journal of American Ceramic Society 88 (2) (2005) 453–455.
[18] D. Zhou, L.X. Pang, J. Guo, Z.M. Qi, T. Shao, X. Yao, C.A. Randall, Phase evolution, phase transition, and microwave dielectric properties of scheelite structured $xBi(Fe_{1/3}Mo_{2/3})O_4-(1-x)BiVO_4$ $(0.0 \leq x \leq 1.0)$ low temperature firing ceramics, Journal of Materials Chemistry 22 (40) (2012) 21412–21419.
[19] D. Zhou, W.G. Qu, C.A. Randall, L.X. Pang, H. Wang, X.G. Wu, J. Guo, G.Q. Zhang, L. Shui, Q.P. Wang, H.C. Liu, X. Yao, Ferroelastic phase transition compositional dependence for solid-solution $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ scheelite-structured microwave dielectric ceramics, Acta Materialia 59 (4) (2011) 1502–1509.
[20] D. Zhou, L.X. Pang, H. Wang, J. Guo, X. Yao, C.A. Randall, Phase transition, Raman spectra, infrared spectra, band gap and microwave dielectric properties of low temperature firing $(Na_{0.5x}Bi_{1-0.5x})(Mo_xV_{1-x})O_4$ solid solution ceramics with scheelite structure, Journal of Materials Chemistry 21 (45) (2011) 18412–18420.
[21] D. Zhou, C.A. Randall, H. Wang, L.X. Pang, Xi 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, Journal of the American Ceramic Society 93 (8) (2010) 2147–2150.
[22] D. Zhou, H. Wang, X. Yao, Y. Liu, Microwave dielectric properties of low-firing $BiNbO_4$ ceramics with V_2O_5 substitution, Journal of Electroceramics 21 (1–4) (2008) 469–472.
[23] S.J. Penn, N.M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, Effect of porosity and grain size on the microwave dielectric properties of sintered alumina, Journal of the American Ceramic Society 80 (7) (1997) 1885–1888.
[24] H. Tamura, Microwave loss quality of $(Zr_{0.8}Sn_{0.2})TiO_4$, American Ceramic Society Bulletin 73 (10) (1994) 92–95.