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A novel low sintering temperature scheelite-structured $CaBiVMoO_8$ microwave dielectric ceramics

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A B S T R A C T

Novel medium-permittivity scheelite-structured $CaBiVMoO_8$ ceramics were prepared by a solid-state reaction route. The effects of sintering temperature on the phase composition, microstructure and microwave dielectric properties of $CaBiVMoO_8$ ceramics were investigated systematically. The Rietveld refinements of X-ray data revealed all samples were well crystallized in space group $I4_1/a$. All the samples exhibited a closely packed grain morphology and discernable grain boundaries. The relationship between microwave dielectric properties and bulk density of samples at different sintering temperatures was further researched. Besides, the lattice energy was one of the important factors affecting the $Q\times f$ values of $CaBiVMoO_8$ ceramics. The temperature coefficient of resonant frequency (τ_f) could be slightly affected by sintering temperature. The $CaBiVMoO_8$ ceramics were expected to be applied to low temperature co-fired ceramics technology. In this paper, the $CaBiVMoO_8$ ceramics exhibited excellent properties sintered at 850 °C for 4h: ε_r ~ 40.55, $Q\times f$ ~ 16,670 GHz, τ_f ~ +55.90 ppm/°C.

1. Introduction

LTCC is an advanced integrated and hybrid circuit packaging technology that has been widely used in many fields, such as high-frequency wireless communication, optical drive and aerospace [1–4]. From the perspective of serializing the permittivity of materials and reducing the size of electronic components, it is of great significance to research and develop ceramic materials with high permittivity that can be co-fired with low melting points electrode materials. Most of them belong to ceramic systems with intermediate permittivity and excellent microwave dielectric properties, such as $BaTi_4O_9$, $Ba_2Ti_9O_{20}$ and $ZnTa_2O_6$. However, most of the above ceramic systems are sintered above 1300 °C, which is difficult to meet the conditions of low temperature co-firing [5–7]. For materials with high inherent sintering temperature, the sintering temperature was reduced by adding a large amount of low-melting additives, which could be cause different degrees of damage to the microwave dielectric properties [8–10].

Most existing scheelite ceramics belong to the low permittivity category. The $CaMoO_4$ is one of the typical scheelite-based ceramic system. The microwave dielectric properties of $CaMoO_4$ ceramics were ε_r ~ 11.7, $Q\times f$ ~ 55,000 GHz, which were sintered at 1100 °C for 4h [11]. The $BiVO_4$ ceramics with the same scheelite structure had excellent microwave dielectric characteristics, ε_r ~ 68, $Q\times f$ ~ 8000 GHz, when sintering temperature was 820 °C [12,13]. Low sintering temperatures and similar ionic radii have made $CaMoO_4$ and $BiVO_4$ ceramics attractive components for the development of LTCC technology [14–16]. However, the low permittivity of the scheelite ceramics is not conducive to miniaturization and modern radar and microwave communications applications. The requirement for intermediate permittivity ceramics is increasing with the development of information technology. However, there are few microwave dielectric ceramic systems with permittivity between 20 and 80, so the development and modification of new intermediate ceramic systems have attracted more and more attention.

In this paper, the invention relates to a novel intermediate permittivity scheelite ceramic ($CaBiVMoO_8$) system with low dielectric loss and low inherent sintering temperature was successfully prepared through the solid-phase reaction. The microstructure, microwave dielectric characteristics and sintering properties of $CaBiVMoO_8$ ceramics were researched.

2. Experimental section

The powder was prepared by mixing $CaCO_3$, Bi_2O_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3 with high purity (>99%) as raw materials according to $CaBiVMoO_8$ formula. The prepared powder mixture was poured into a nylon tank with ethanol and ground for 4h. The ground mixture was calcined for 4h at 650 °C after drying. Then the calcined mixture was ground for another 4h, dried, mixed with 5 wt% paraffin, and pressed at 100MPa to make a cylinder with a thickness of 4 ~ 5mm and a diameter of 10mm. It was sintered at a temperature of 775 °C–875 °C for 4h to obtain $CaBiVMoO_8$ ceramics.

The Rigaku D/max 2550 PC was used to detect the phase composition and crystal structure of $CaBiVMoO_8$ ceramics. The XRD was obtained using a step-scan method at a speed of 0.02°/s between 10° and 70°(2θ). To better understand the structure of the samples, the XRD data was refined by the Fullprof software. The microstructure of the $CaBiVMoO_8$ ceramics was obtained by scanning electron microscopy (ZEISS MERLIN Compact, Germany). The permittivity

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and $Q \times f$ of all $CaBiVMoO_8$ ceramics were detected through the network analyzer (N5234A, Agilent Co, America). The bulk density of the $CaBiVMoO_8$ ceramics was measured through the Archimedes method.

In the temperature range of 25 °C–85 °C, the value of τ_f was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(T_{85} - T_{25})} \times 10^{6(ppm/^\circ C)} \quad (1)$$

where f_{85} and f_{25} represented the resonant frequencies at the temperature of T_{85} and T_{25}, respectively.

3. Results and discussion

The scheelite structure compounds usually have a wide cationic mineral structure solubility. The radius of Bi^{3+} ion (1.17 Å) is similar to Ca^{2+} ion (1.12 Å). Besides, the radius of V^{5+} ion (0.355 Å) is similar to the radius of Mo^{6+} ion (0.41 Å). Through ion substitution, intrinsic stress can be introduced into the $BiVO_4$ ceramics with monoclinic scheelite structure, which changes the $BiVO_4$ ceramics from monoclinic phase to tetragonal phase [17–19]. Fig. 1 shows the XRD patterns of $CaBiVMoO_8$ ceramics sintered at 775 °C–875 °C for 4h. It can be found that the phase composition of the $CaBiVMoO_8$ ceramics is similar to the $CaMoO_4$ structure (PDF #85-0585: Tetragonal, $I4_1/a$), which is consistent with the results of the research of $CaBiVMoO_8$ by Cortés et al. [20,21]. All the results show that the phase composition and crystal structure of $CaBiVMoO_8$ does not change significantly at different sintering temperatures.

Fig. 2 shows the Rietveld refinement result of $CaBiVMoO_8$ ceramics sintered at 850 °C for 4h. The sample was confirmed as the scheelite structure (Tetragonal: $I4_1/a$, No.88) after refinement. The strongest diffraction peaks for all samples were greater than 10,000 to reduce the effect of noise on the results. Besides, Table .1 shows the Rietveld refinement parameters. The Rietveld discrepancy factors R_p and R_{wp} are 7.05% and 6.96%. The refined values of lattice parameters of the sample sintered at 850 °C for 4h are $a = b = 5.1857$ Å, $c = 11.5752$ Å, and $V = 311.3658$ Å^3.

Fig. 3(a)–(e) shows the SEM pictures of $CaBiVMoO_8$ ceramics sintered at different sintering temperatures. All the ceramics show a dense microstructure with few pores. The microstructure of the sample sintered at 775 °C is relatively dense, but the grain size is small. As shown, the grain size of the samples tends to increase when the sintering temperature increases. However, for microwave dielectric characteristics, the size of the grain size does not completely determine the properties of ceramics. Fig. 3(e) displays that excessive sintering temperature may cause abnormal growth of grains and uneven size, which will reduce the performance of $CaBiVMoO_8$ ceramics. Therefore, Fig. 3(d) shows that the microstructure of $CaBiVMoO_8$ ceramics sintered at 850 °C for 4h is dense, and the grain size is uniform. The SEM pictures phenomenon is completely consistent with the Rietveld refinement results.

Fig. 4 shows the bulk density, ε_r and $Q \times f$ values of $CaBiVMoO_8$ ceramics sintered at various temperatures for 4h. When the sintering temperature increases, the bulk density of ceramics increases and reaches a peak when the temperature achieves 850 °C. As the sintering temperature continues to increase, the bulk density begins to decrease. Abnormal grain growth and uneven grain size reduce the density of $CaBiVMoO_8$ ceramics. The trend of permittivity is similar to bulk density. Generally, the permittivity primarily is involved with the ionic polarizability, second phase and density of ceramics [22,23]. The permittivity of $CaBiVMoO_8$ ceramics increases gradually when the sintering temperature increases, and reaches a peak when the temperature achieves 850 °C. As the sintering temperature continues to increase, the permittivity begins to decrease. The change of the permittivity of the ceramics is involved with the change of the bulk density, which indicates that density is

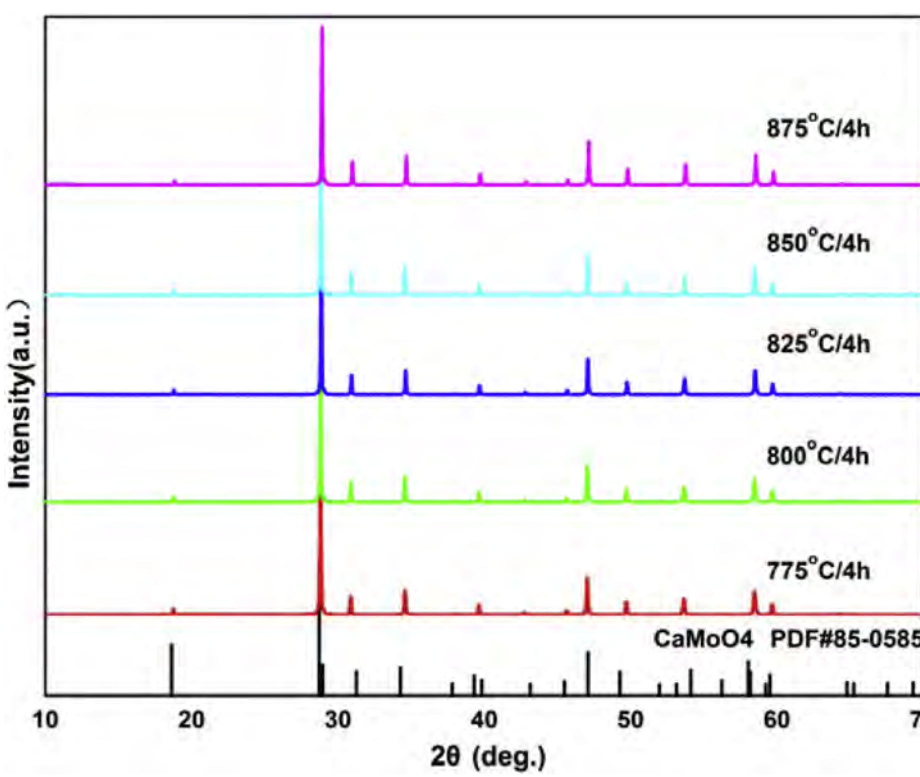

Fig. 1. The XRD patterns of $CaBiVMoO_8$ ceramics sintered at various temperatures for 4h.

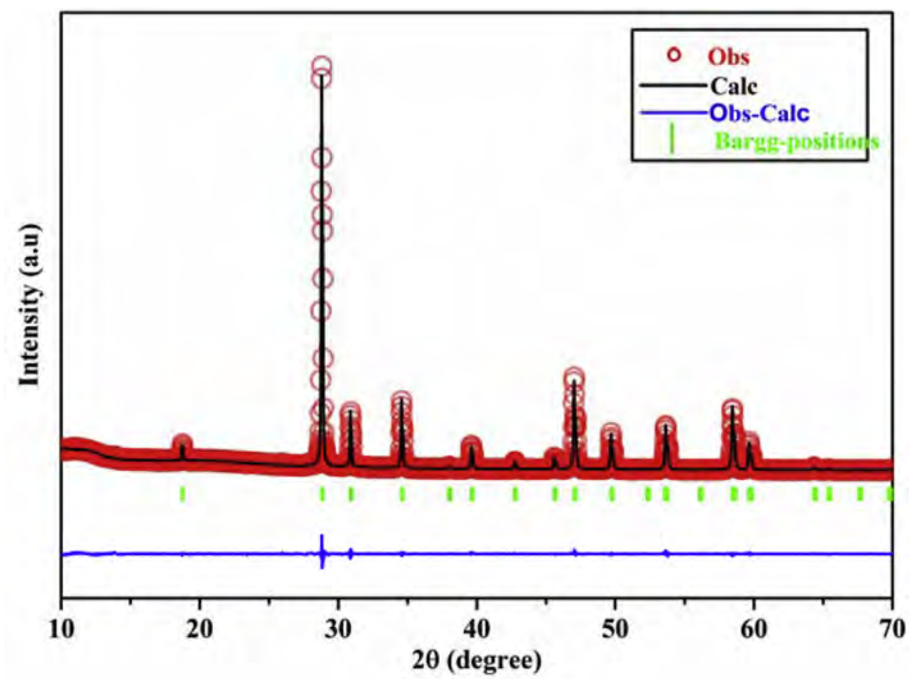

Fig. 2. The Rietveld refinement plot of $CaBiVMoO_8$ ceramics sintered at 850 °C for 4h.

Table 1
Refined structural parameters and reliability factors of $CaBiVMoO_8$ ceramics sintered at different temperatures.

S.T.(°C)	R_p(%)	R_{wp}(%)	a = b(Å)	c(Å)	α = β = γ(°)	V(Å)
775	14.1	10.8	5.1787	11.5631	90°	310.1097
800	7.45	7.89	5.1789	11.5659	90°	310.2131
825	10.3	10.5	5.1801	11.5659	90°	310.3459
850	7.05	6.96	5.1865	11.5752	90°	311.3658
875	8	8.28	5.1857	11.5752	90°	311.2779

S.T.– the sintering temperature of $CaBiVMoO_8$ ceramics.
R_p– reliability factor of patterns.
R_{wp}– reliability factor of the weighted pattern.

one of the main factors affecting the permittivity. The intrinsic and extrinsic factors determine the $Q\times f$ values of microwave dielectric ceramics. Intrinsic losses are involved with the lattice structure, while extrinsic losses are usually involved with the second phase, porosity, grain size [24–30]. As shown in Fig. 1, no secondary phase were detected in all samples. The trend of $Q\times f$ values is similar to the bulk density, indicating that the $Q\times f$ is mainly dependent on the bulk density. The $Q\times f$ values of ceramics increases gradually when the sintering temperature increases, and reaches the maximum value when the temperature achieves 850 °C. The $Q\times f$ values begin to decrease as the temperature increases constantly.

The calculation formula of the $CaBiVMoO_8$ ceramics lattice energy is as follows [31–33]:

$$U_{Total} = \sum_{\mu}(U_{bi}^{\mu} + U_{bc}^{\mu}) \tag{2}$$

$$U_{bc}^{\mu} = 2100m\frac{(Z_{+}^{\mu})^{1.64}}{(d^{\mu})^{0.75}}f_c^{\mu} \tag{3}$$

$$U_{bi}^{\mu} = 1270\frac{(m+n)Z_{+}^{\mu}Z_{-}^{\mu}}{d^{\mu}}\left(1 - \frac{0.4}{d^{\mu}}\right)f_i^{\mu} \tag{4}$$

where Z_{+}^{μ} and Z_{-}^{μ} are the valence states of cations and anions which constituted bond μ. U_{bc}^{μ} are the covalent part and U_{bi}^{μ} are the ionic part of the μ bond. Lattice energy U characterizes the binding ability between cations and anions. The crystal structure with high binding energy indicates that the crystal structure has high stability and low intrinsic loss [34]. Therefore, Lattice energy can be used to analyze the $Q\times f$ values of microwave dielectric ceramics. Also, a lower loss can be predicted for the compounds with larger lattice energy. Fig. 5 shows the lattice energy and $Q\times f$ values of $CaBiVMoO_8$ ceramics sintered at various temperatures. The $Q\times f$ values show a similar trend to the chemical bond lattice energy, which indicates that lattice energy is one of the important factors affecting the $Q\times f$ values of $CaBiVMoO_8$ ceramics.

In this work, the τ_f values of $CaBiVMoO_8$ ceramics sintered at various sintering temperature have little change. This shows that the sintering temperature has little effect on the τ_f of $CaBiVMoO_8$ ceramics. The τ_f value of the $CaBiVMoO_8$ ceramics sintered at 850 °C for 4h was +54.90 ppm/°C. In conclusion, the $CaBiVMoO_8$ samples achieved superior microwave dielectric properties of ε_r ~ 40.55, $Q\times f$ ~ 16,670 GHz, τ_f ~ +54.90 ppm/°C sintered at 850 °C for 4h.

4. Conclusions

The novel medium-permittivity $CaBiVMoO_8$ ceramics with low inherent sintering temperature and low dielectric loss were successfully prepared by the solid-state reaction route. In this paper, the influences of sintering temperature on the microwave dielectric characteristics, the microstructure, and crystal structure of $CaBiVMoO_8$ ceramics were systematically researched. The research found that the permittivity, $Q\times f$ values and bulk density of the samples had similar trends with the sintering temperature. Lattice energy was one of the important factors affecting the $Q\times f$ values of $CaBiVMoO_8$ ceramics. The τ_f values of $CaBiVMoO_8$ ceramics did not change significantly at different sintering temperatures. The $CaBiVMoO_8$ ceramics achieved prominent microwave dielectric properties of ε_r ~ 40.55, $Q\times f$ ~ 16,670 GHz, τ_f ~ +55.90 ppm/°C when the sintered temperature reached 850 °C, which could be applied to LTCC technology in the future.

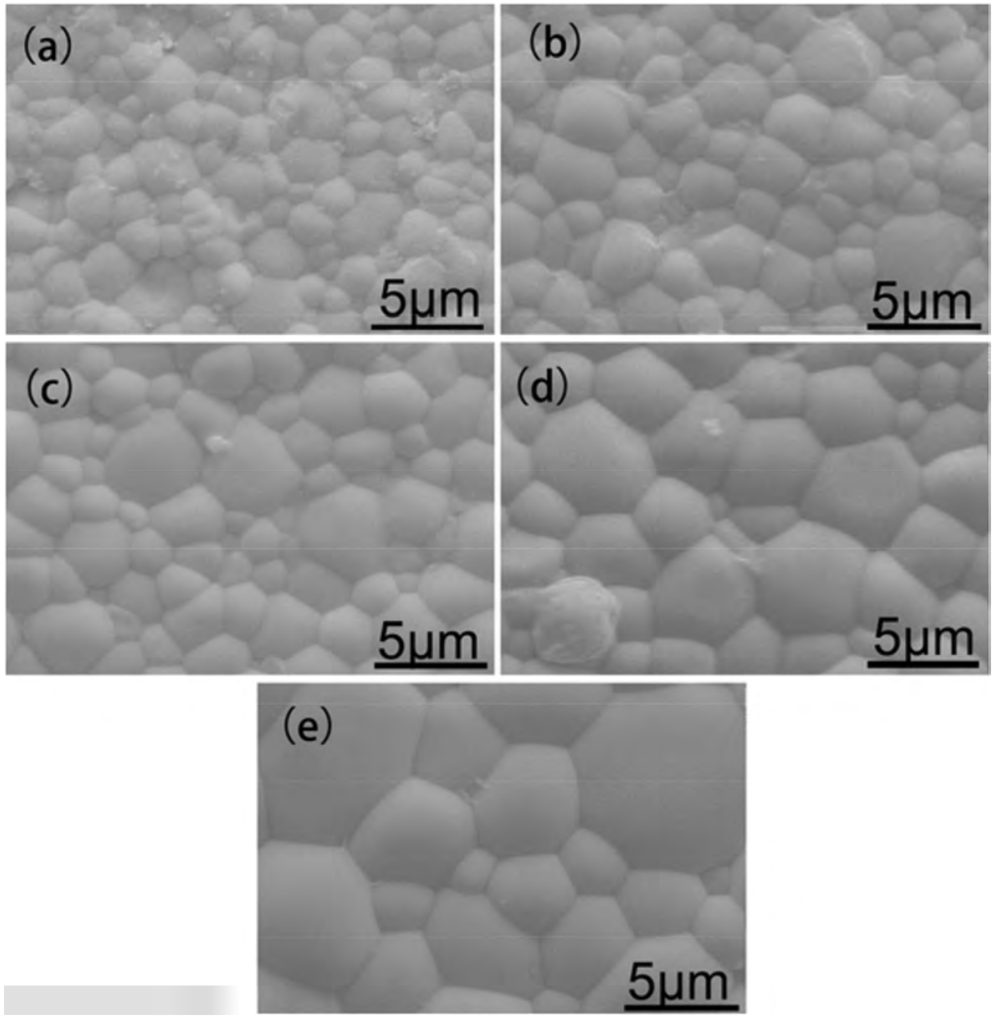

Fig. 3. The SEM micrographs of $CaBiVMoO_8$ ceramics sintered at various sintering temperatures for 4h: (a) 775 °C, (b) 800 °C, (c) 825 °C, (d) 850 °C, (e) 875 °C.

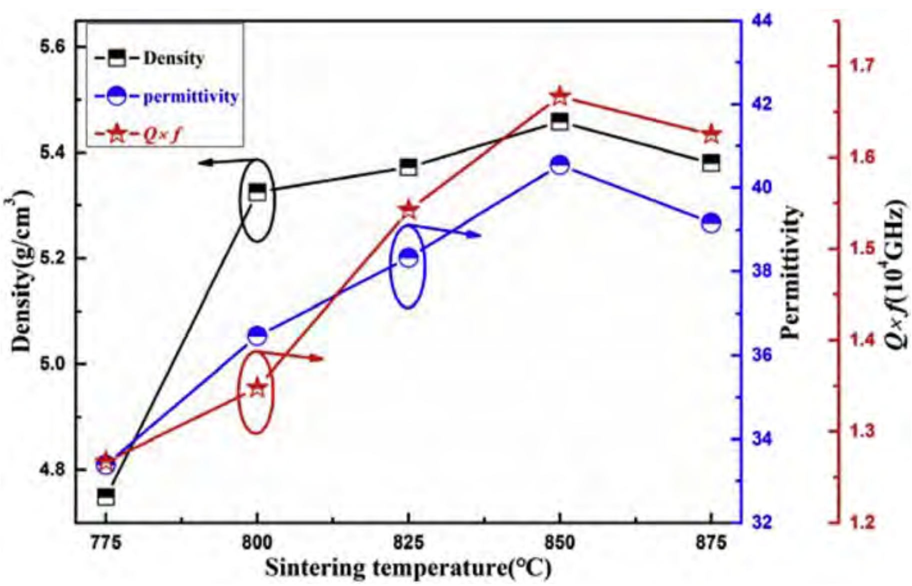

Fig. 4. The bulk density, ε_r and $Q\times f$ values of $CaBiVMoO_8$ ceramics sintered at various temperatures for 4h.

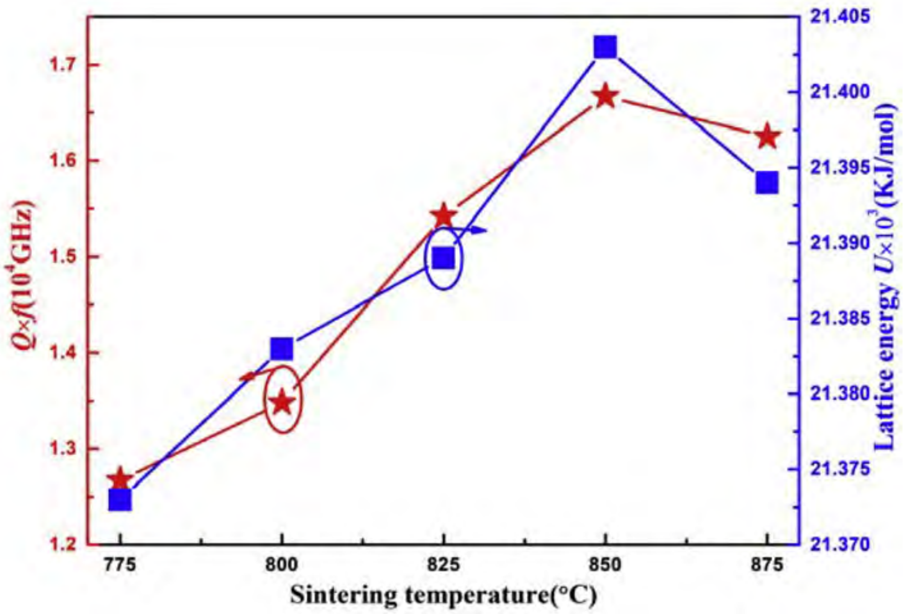

Fig. 5. The chemical bond lattice energy and $Q\times f$ values of $CaBiVMoO_8$ ceramics sintered at various temperatures for 4h.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] I.M. Reaney, D. Iddles, Microwave dielectric ceramics for resonators and filters in mobile phone networks, J. Am. Ceram. Soc. 89 (2006) 2063–2072.
[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, D.W. Wang, C. Li, B.B. Jin, I.M. Reaney, High permittivity and low loss microwave dielectrics suitable for 5G resonators and low temperature cofired ceramic architecture, J. Mater. Chem. C 5 (2017) 10094–10098.
[4] W. Wersing, Microwave ceramics for resonators and filters, Curr. Opin. Solid St. M. 1 (1996) 715–731.
[5] M.T. Sebastian, New low loss microwave dielectric ceramics in the BaO-TiO_2-Nb_2O_5/Ta_2O_5 system, J. Mater. Sci. Mater. Electron. 10 (1999) 475–478.
[6] T. Negas, G. Yeager, S. Bell, et al., $BaTi_4O_9$/$Ba_2Ti_9O_{20}$-based ceramics resurrected form modern microwave applications, J. Am. Ceram. Soc. 72 (1993) 80–89.
[7] N. Michiura, T. Tatekawa, Y. Higuchi, H. Tamara, Role of donor and acceptor ions in the dielectric loss tangent of $(Zr_{0.8}Sn_{0.2})TiO_4$ dielectric resonator material, J. Am. Ceram. Soc. 78 (1995) 793–796.
[8] P. Zhang, X.Y. Zhao, Y.G. Zhao, Effects of MBS addition on the low temperature sintering and microwave dielectric properties of $Li_3Mg_2NbO_6$ ceramics, J. Mater. Sci. Mater. Electron. 27 (2016) 6395–6398.
[9] P. Zhang, J.W. Liao, Y.G. Zhao, X.Y. Zhao, M. Xiao, Effects of B_2O_3 addition on the sintering behavior and microwave dielectric properties of $Li_3Mg_2NbO_6$ ceramics, J. Mater. Sci. Mater. Electron. 28 (2017) 686–690.
[10] P. Zhang, H. Xie, Y.G. Zhao, X.Y. Zhao, M. Xiao, Low temperature sintering and microwave dielectric properties of $Li_3Mg_2NbO_6$ ceramics doped with Li_2O-B_2O_3-SiO_2 glass, J. Alloys Compd. 690 (2017) 688–691.
[11] G.K. Choi, S.Y. Cho, J.S. An, K.S. Hong, Microwave dielectric properties and sintering behaviors of scheelite compound $CaMoO_4$, J. Eur. Ceram. Soc. 26 (2006) 2011–2015.
[12] 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.
[13] L.X. Pang, D. Zhou, W.G. Liu, Z.M. Qi, Z.X. Yue, Crystal structure and microwave dielectric behaviors of scheelite structured (1-x)$BiVO_4$-x$La_{2/3}MoO_4$(0.0≤x≤1.0) ceramics with ultra-low sintering temperature, J. Eur. Ceram. Soc. 38 (2018) 1535–1540.
[14] G.K. Choi, J.R. Kim, S.H. Yoon, K.S. Hong, Microwave dielectric properties of scheelite (A = Ca, Sr, Ba) and wolframite (A = Mg, Zn, Mn) $AMoO_4$ compounds, J. Eur. Ceram. Soc. 27 (2007) 3063–3067.
[15] Z.L. Ma, J.X. Zhao, D. Zhou, Microwave dielectric properties of the (1-x) $La(Nb_{0.9}V_{0.1})O_4$-x$CaMoO_4$(0.05≤x≤0.50) scheelite solid solution ceramics, J. Alloys Compd. 789 (2019) 345–350.
[16] L.X. Pang, D. Zhou, Z.X. Yue, Temperature independent low firing $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (0.2≤x≤0.8) microwave dielectric ceramics, J. Alloys Compd. 781 (2019) 385–388.
[17] 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 Mater. 59 (2011) 1502–1509.
[18] R.M. Hazen, J.W.E. Mariathasan, Bismuth Vanadate: a high-pressure, high-temperature crystallographic study of the ferroelastic-paraelastic transition, Science 216 (1982) 991–993.
[19] 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 structures, J. Mater. Chem. 21 (2011) 18412–18420.
[20] L.M.C. Cortés, D.B. Hernández-Uresti, S. Obregón, S. Mejía-Rosales, Synthesis and characterization of $CaBiVMoO_8$ as a novel visible-light-driven photocatalyst, Mater. Lett. 189 (2017) 164–167.
[21] L.M.C. Cortés, D.B. Hernández-Uresti, S. Obregón, S. Mejía-Rosales, Photocatalytic performance of $CaBiVMoO_8$ catalysts for orange G and rhodamine B degradation, Res. Chem. Intermed. 43 (2017) 5727–5739.
[22] R.D. Shannon, G.R. Rossman, Permittivitys of silicate garnets and the oxide additivity rule, Am. Mineral. 77 (1992) 94–100.
[23] E.S. Kim, S.H. Kim, K.H. Yoon, Dependence of thermal stability on octahedral distortion of (1-x)$(Ca_{0.3}Li_{0.119}Sm_{0.427})TiO_3$-x$LnAlO_3$(Ln=Nd, Sm) ceramics, Ceram. Soc. Jpn 112 (2004) 1645–1649.
[24] S.H. Yoon, D.W. Kim, S.Y. Cho, K.S. Hong, Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds, J. Eur. Ceram. Soc. 26 (2006) 2051–2054.
[25] S.D. Ramarao, S.R. Kiran, V.R.K. Murthy, Structural, lattice vibrational, optical and microwave dielectric studies on $Ca_{1-x}Sr_xMoO_4$ ceramics with scheelite structure, J. Mater. Res. Bull. 56 (2014) 71–79.
[26] C.L. Huang, S.S. Liu, Low-loss microwave dielectrics in the $(Mg_{1-x}Zn_x)_2TiO_4$ ceramics, Am. Ceram. Soc. 91 (2008) 3428–3430.
[27] C.L. Huang, J.Y. Chen, High-Q microwave dielectrics in the $(Mg_{1-x}Co_x)_2TiO_4$ ceramics, J. Am. Ceram. Soc. 92 (2009) 379–383.
[28] C.L. Huang, J.Y. Chen, Low-loss microwave dielectric ceramics using $(Mg_{1-x}Mn_x)_2TiO_4$ (x=0.02-0.1) solid solution, J. Am. Ceram. Soc. 92 (2009) 675–678.
[29] C.L. Huang, W.R. Yang, P.C. Yu, High-Q microwave dielectrics in low-temperature sintered $(Zn_{1-x}Ni_x)_3Nb_2O_8$ ceramics, J. Eur. Ceram. Soc. 34 (2014) 277–284.
[30] P. Zhang, Y.G. Zhao, Effects of structural characteristics on microwave

dielectric properties of $Li_2Mg(Ti_{1-x}Mn_x)_3O_8$ ceramics, J. Alloys Compd. 647 (2015) 386–391.
[31] D.F. Xue, S.Y. Zhang, Calculation of the nonlinear optical coefficient of the $NdAl_3(BO_3)_4$ crystal, J. Phys. Condens. Matter 8 (1996) 1949–1956.
[32] Z.J. Wu, Q.B. Meng, S.Y. Zhang, Semi empirical study on the valences of Cu and bond covalency in $Y_{1-x}CaxBa_2Cu_3O_{6+y}$, Phys. Rev. B 58 (1998) 958–962.
[33] Q.B. Meng, Z.J. Wu, S.Y. Zhang, Evaluation of the energy barrier distribution in many-particle systems using the path integral approach, J. Phys. Condens. Matter 10 (1998) 85–88.
[34] H.Y. Yang, S.R. Zhang, Y.W. Chen, H.C. Yang, Y. Yuan, E.Z. Li, Crystal chemistry, Raman spectra, and bond characteristics of trirutile-type $Co_{0.5}Ti_{0.5}TaO_4$ microwave dielectric ceramics, Inorg. Chem. 58 (2019) 968–976.

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