Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 4574–4577

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Novel glass-free low-temperature fired microwave dielectric ceramics: $Bi(Ga_{1/3}Mo_{2/3})O_4$

Li-Xia Pang[a], Wei-Guo Liu[a], Di Zhou[b,*], Zhen-Xing Yue[c]

[a]Laboratory of Thin Film Techniques and Optical Test, Xi'an Technological University, Xi'an 710032, Shaanxi, China
[b]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China
[c]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Received 18 September 2015; received in revised form 7 November 2015; accepted 26 November 2015
Available online 3 December 2015

Abstract

Novel glass-free low temperature firing microwave dielectric ceramics, $Bi(Ga_{1/3}Mo_{2/3})O_4$, with ordered scheelite structure, were prepared through a conventional solid state reaction method. Dense ceramics were prepared at sintering temperatures from 800 to 860 °C. The $Bi(Ga_{1/3}Mo_{2/3})O_4$ compound was crystallized with B-site ordered Scheelite-type structure with space group C2/c. The $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics can be well sintered at about 830 °C, exhibiting good microwave dielectric properties of $\varepsilon_r \sim 26.1$, Qf ~ 49,800 GHz, and TCF ~ −86 ppm/°C. Intrinsic dielectric parameters of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics were estimated by fitting far-infrared (FIR) reflectance spectra with the classical harmonic oscillator model.

Keywords: A: Sintering; B: Spectroscopy; C: Dielectric properties

1. Introduction

Low temperature co-fired ceramics (LTCC) technology provides an elegant and cost-effective way for 3D integration of electronic components used in mainframe computer and telecommunication systems. LTCC technology relies on microwave dielectric ceramics that could be densified at temperatures lower than the melting temperature of the metals (such as Ag, Cu, and Al, etc) used in the internal circuitry, without scarifying their dielectric performance. Hence, the search for microwave dielectric ceramic materials, with high quality factor (Qf value), near zero temperature coefficient of resonant frequency (TCF value) and low sintering temperature (S.T.), has been a hot research topic all over the world [1–3]. Since the $BaTe_4O_9$ microwave dielectric ceramic with a sintering temperature of about 550 °C was reported by Kwon et al. [4,5], various microwave dielectric ceramics with ultra-low sintering temperatures have been explored [6–13]. In our previous works, monoclinic scheelite structured $Bi(Fe_{1/3}Mo_{2/3})O_4$, in which the FeO_4 and MoO_4 tetrahedrons take an ordered arrangement, was found to be well densified at about 830 °C and displayed high microwave dielectric properties [14,15]. Similar to $Bi(Fe_{1/3}Mo_{2/3})O_4$, $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic could be well densified at 840 °C, with a permittivity of 25.2, Qf value of 40,000 GHz and TCF value of 65 ppm/°C [16]. A similar ordered scheelite structure has also been found in $Bi(Ga_{1/3}Mo_{2/3})O_4$ and $Bi(Sc_{1/3}Mo_{2/3})O_4$, while an analogous phase could not be formed if aluminum (Al) or chromium (Cr) was contained at the B site [17,18]. In the present work, $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics were prepared by using the solid state reaction method. Phase structure, microstructure, microwave dielectric properties, and intrinsic dielectric properties of the ceramics were studied in detail.

2. Experimental procedure

Proportionate amounts of reagent-grade Bi_2O_3 (> 99%, Shu-Du Powders Co. Ltd., Chengdu, China), Ga_2O_3 (> 99%, Sinopharm

*Corresponding author. Tel./fax: +86 29 82668679.
E-mail address: zhoudi1220@gmail.com (D. Zhou).

http://dx.doi.org/10.1016/j.ceramint.2015.11.152
0272-8842/

Chemical Reagent Co., Ltd, Shanghai, China), and MoO_3 (> 99%, Fuchen Chemical Reagents, Tianjin, China) were measured according to the stoichiometric formulation of $Bi(Ga_{1/3}Mo_{2/3})O_4$. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) with a running speed of 400 rpm. The mixture was dried and calcined at 700 °C for 4 h. The calcined powders were ball milled again for 5 h with a running speed of 450 rpm. After drying, the powders were pressed into cylinders (10 mm in diameter and 4–5 mm in height) under a uniaxial pressure of 20 MPa. Samples were sintered in the temperature range from 770 °C to 860 °C for 2 h. To measure crystalline structure, the sintered pellets were crushed into powder. X-ray diffraction (XRD) was performed by using a XRD with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). To examine grain morphology, the as-fired samples were observed by using scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Room temperature Far-infrared reflectivity spectra were measured by using a Bruker IFS 66v FTIR spectrometer. Dielectric properties at microwave frequencies were measured according to the $TE_{01\delta}$ dielectric resonator method with a network analyzer (HP 8720 Network Analyzer, Hewlett–Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). Temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$\mathrm{TCF}(\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \ \mathrm{ppm/^oC}, \quad (1)$$

where f_T and f_{T_0} are the $TE_{01\delta}$ resonant frequencies at temperature T and T_0, respectively.

3. Results and discussion

According to references [14,17], $Bi(Ga_{1/3}Mo_{2/3})O_4$ compound could crystallize as B-site ordered or disordered Scheelite-type structure, depending on heating temperature. B-site ordered superstructure could be obtained at temperatures above 700 °C. Fig. 1 shows XRD patterns of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics sintered at 830 and 860 °C for 2 h. Line splitting and superstructure diffraction peaks were observed. Pure monoclinic B-site ordered scheelite structure with space group C2/c was formed, when the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics were sintered at temperatures of ≥ 830 °C. The lattice parameters of $Bi(Ga_{1/3}Mo_{2/3})O_4$ prepared at 860 °C were $a=16.15$, $b=11.65$, $c=5.25$ and $\beta=91.01°$.

Fig. 2(a) presents bulk densities of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics as a function of sintering temperature. The bulk density increased to a saturated value when the sintering temperature increased to 800 °C. Surface SEM photograph of the as-fired $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic is shown in Fig. 3. It has a dense and homogeneous microstructure, after it was sintered at 830 °C for 2 h. The grain size was between 1 and 2 μm. Both the bulk density and microstructure results indicated that the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic had been densified well. As shown in Fig. 2(a), when the sintering temperature was increased to 860 °C, bulk density of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic was decreased slightly. It can be attributed the volatilization of the

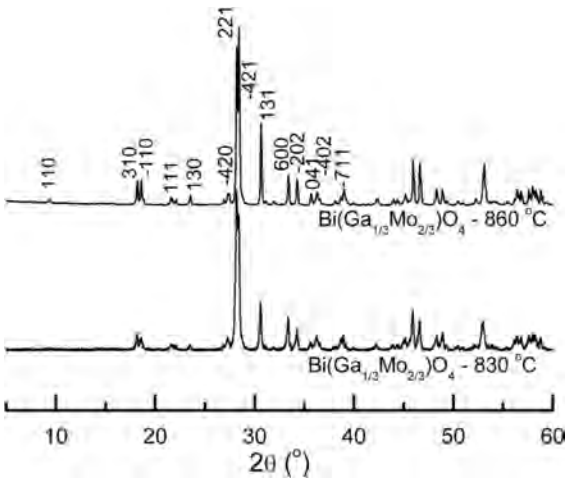

Fig. 1. XRD patterns of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ samples sintered at 830 and 860 °C for 2 h.

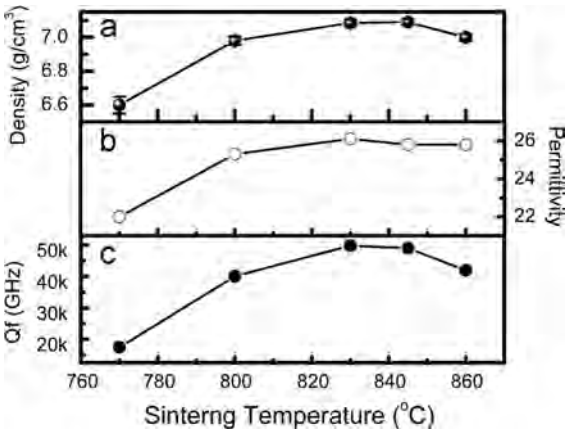

Fig. 2. Bulk density (a), microwave dielectric permittivity (b) and Qf value (c) of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics as a function of sintering temperature.

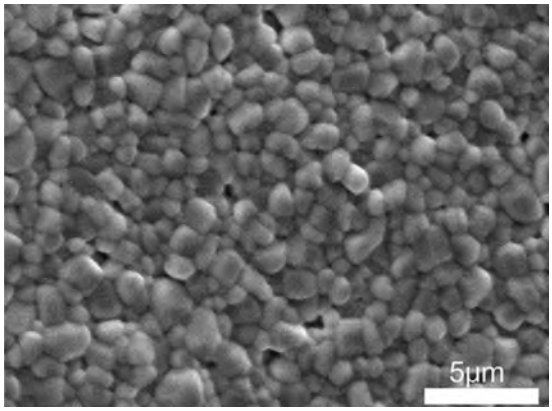

Fig. 3. Surface SEM photograph of the as-fired $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics sintered at 830 °C for 2 h.

content with low melting temperature and the internal pores formed at higher sintering temperature.

Fig. 2(b) and (c) show microwave dielectric permittivity and Qf value of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics as a function of

sintering temperature, respectively. The variation of permittivity with sintering temperature was similar to that of bulk density. The permittivity has increased with sintering temperature and reached a maximum value of 26.1 at 830 °C, which was resulted from the disappearance of pores. The permittivity was decreased to 25.8 when the sintering temperature was increased to 845 and 860 °C. The increase of the internal pores resulted in the decrease in permittivity. The maximum Qf value was 49,800 GHz in the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic sintered at 830 °C for 2 h, as shown in Fig. 2(c).

Resonant frequency and Qf value of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics measured in the temperature range of 25–125 °C with the $TE_{01\delta}$ dielectric resonator method are shown in Fig. 4. Microwave permittivity of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic increased linearly from 26.1 to 26.5, when the measuring temperature was increased from RT (room temperature, 25 °C) to 120 °C. Correspondingly, the resonant frequency decreased linearly with measuring temperature. TCF value calculated with formula (1) was −86 ppm/°C. The Qf value was between 40,000 and 50,000 GHz in the temperature range of 25–125 °C.

With Far-infrared (FIR) reflectivity spectrum, complex dielectric spectrum of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramic was obtained according to the relationship between reflectivity $R(\omega)$ and complex dielectric, (Eq. (2)) and fitting method of classical harmonic oscillator model (Eq. (3)).

$$R(\omega) = \left| \frac{1-\sqrt{\varepsilon*(\omega)}}{1+\sqrt{\varepsilon*(\omega)}} \right|^2, \tag{2}$$

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j\omega}, \tag{3}$$

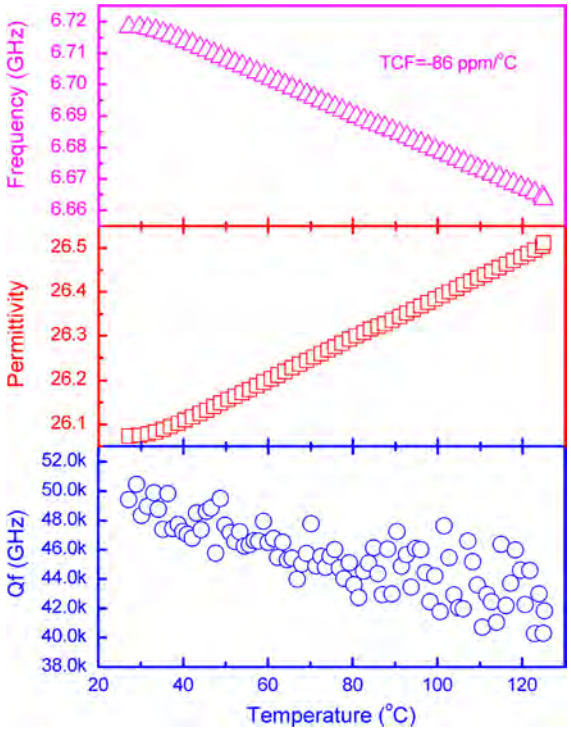

Fig. 4. Resonant frequency, dielectric permittivity and Qf value of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics sintered at 830 °C for 2 h.

where $\varepsilon^*(\omega)$ is complex dielectric function, ε_∞ is the dielectric constant caused by the electronic polarization at high frequencies, γ_j, ω_{oj} and ω_{pj} are the damping factor, the transverse frequency and plasma frequency of the j-th Lorentz oscillator, respectively and n is the number of transverse phonon modes.

The measured and fitted FIR reflectivity spectra are shown in Fig. 5(a), while the real and imaginary parts of the complex dielectric are shown in Fig. 5(b) and (c), respectively. According to factor group analysis, the predicted vibration modes of $Bi(Ga_{1/3}Mo_{2/3})O_4$ with C2/c symmetry at Γ point is as follows:

$$\Gamma = 26A_g(R) + 28B_g(R) + 25A_u(I) + 26B_u(I) \tag{4}$$

where $26A_g$ and $28B_g$ are the Raman active modes, while $25A_u$ and $26B_u$ are Infrared active modes. As shown in Fig. 5 (a), the number of the experimentally observed modes is lower than the symmetry prediction. A_u and B_u modes may not be entirely resolved because the anisotropy could have been averaged [19]. Moreover, since the vibrational spectra depend primarily on local environment and symmetry and they are more sensitive to short range order [11], some vibrational modes could have been broadened and some of them might have been smeared out, because of the short range disordering in the monoclinic scheelite structure of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics. In this work, twenty-six Lorentz oscillator modes

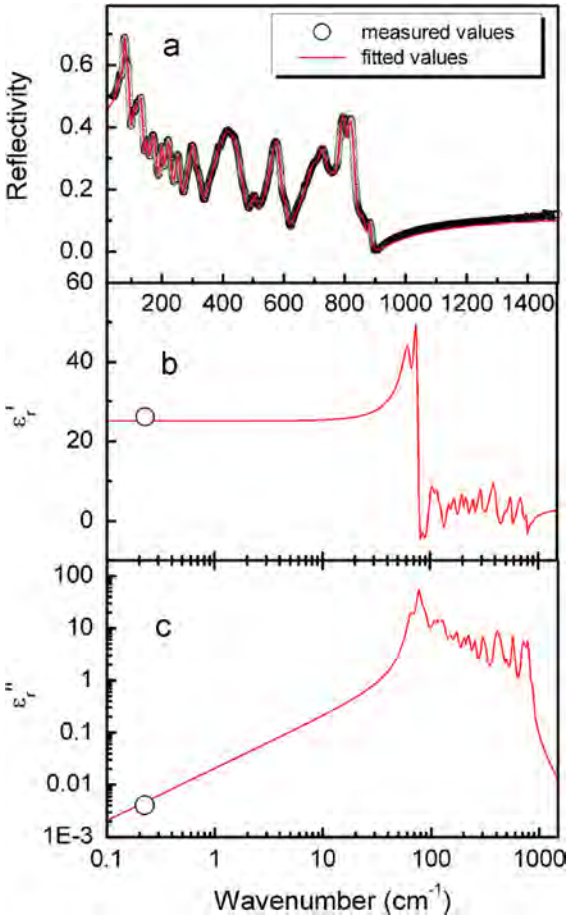

Fig. 5. Measured and fitted FIR reflectivity spectra and complex dielectric spectrum of the $Bi(Ga_{1/3}Mo_{2/3})O_4$ ceramics.

were used for fitting, leading to a fitted ε_∞ to be 4.55. It was found that both the calculated dielectric permittivity (the real part of the complex dielectric) and dielectric loss values (the imaginary part of the complex dielectric) at microwave frequencies were almost equal to those measured by using $TE_{01\delta}$ method. It can be deduced that the polarization of the Bi$(Ga_{1/3}Mo_{2/3})O_4$ ceramics at microwave frequencies was mainly attributed to the absorptions of phonon oscillation at infrared region.

4. Conclusions

A low temperature firing microwave dielectric ceramics, Bi$(Ga_{1/3}Mo_{2/3})O_4$, with B site ordered scheelite structure, has been synthesized by using a solid state reaction method. Well densified ceramics could be obtained from 800 to 860 °C. The Bi$(Ga_{1/3}Mo_{2/3})O_4$ ceramics sintered at 830 °C for 2 h possessed promising microwave dielectric properties, with a permittivity of 26.1, a high Qf value of 49,800 GHz and a TCF value of −86 ppm/°C. Polarization of the Bi$(Ga_{1/3}Mo_{2/3})O_4$ ceramics at microwave frequencies was mainly attributed to the absorptions of phonon oscillation at infrared region.

Acknowledgments

This work was supported by the National Natural Science foundation of China (51202182 and 51202178), the Natural Science Foundation of Shaanxi Province (2014JQ6200), the Young Star Project of Science and Technology of Shaanxi Province (2015KJXX-39) and open project of the State Key Laboratory of New Ceramic and Fine Processing (Tsinghua University). The authors would like to thank the administrators in IR beamline workstation of National Synchrotron Radiation Laboratory (NSRL) for their help in the IR measurement.

References

[1] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, Int. Mater. Rev. 53 (2008) 57–90.
[2] A.K. Axelsson, N.M. Alford, Bismuth titanates candidates for high permittivity LTCC, J. Eur. Ceram. Soc. 26 (2006) 1933–1936.
[3] 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.
[4] D.K. Kwon, M.T. Lanagan, T.R. Shrout, Microwave dielectric properties of BaO–TeO_2 binary compounds, Mater. Lett. 61 (2007) 1827–1831.
[5] 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.
[6] G. Subodh, M.T. Sebastian, Glass-free $Zn_2Te_3O_8$ microwave ceramic for LTCC applications, J. Am. Ceram. Soc. 90 (2007) 2266–2268.
[7] A. Feteira, D.C. Sinclair, Microwave dielectric properties of low firing temperature $Bi_2W_2O_9$ Ceramics, J. Am. Ceram. Soc. 91 (2008) 1338–1341.
[8] 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.
[9] 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.
[10] D. Zhou, C.A. Randall, L.X. Pang, H. Wang, J. Guo, G.Q. Zhang, X.G. Wu, L. Shui, X. Yao, Microwave dielectric properties of Li_2WO_4 ceramic with ultra-low sintering temperature, J. Am. Ceram. Soc. 94 (2011) 348–350.
[11] S.E. Kalathil, U.A. Neelakantan, R. Ratheesh, Microwave dielectric properties of ultralow-temperature cofirable $Ba_3V_4O_{13}$ ceramics, J. Am. Ceram. Soc. 97 (2014) 1530–1533.
[12] G. Schileo, A. Dias, R.L. Moreira, T.J. Jackson, P.A. Smith, K.T. S. Chung, A. Feteira, Structure and microwave dielectric properties of low firing $Bi_2Te_2W_3O_{16}$ ceramics, J. Am. Ceram. Soc. 97 (2014) 1096–1102.
[13] C.F. Tseng, P.A. Lin, Microwave dielectric properties of novel glass-free low-firing Li_2CeO_3 ceramics, J. Am. Ceram. Soc. 97 (2014) 1020–1022.
[14] By. W. Jeitschko, A.W. Sleight, W.R. McClellan, J.F. Weiher, A. Comprehensive, Study of disordered and ordered Scheelite-related $Bi_3(FeO_4)(MoO_4)_2$, Acta Crystallogr. B: Struct. Sci. 32 (1976) 1163–1170.
[15] D. Zhou, L.X. Pang, J. Guo, Y. Wu, G.Q. Zhang, H. Wang, X. Yao, Sintering behavior and microwave dielectric properties of novel low temperature firing $Bi_3FeMo_2O_{12}$ ceramic, J. Adv. Dielec. 1 (2011) 379–382.
[16] L.X. Pang, D. Zhou, J. Guo, Z.M. Qi, T. Shao, Microwave dielectric properties of scheelite structured low temperature fired Bi$(In_{1/3}Mo_{2/3})O_4$ ceramic, Ceram. Int. 39 (2013) 4719–4722.
[17] A.W. Sleight, W. Jeitschko, $Bi_3(FeO_4)(MoO_4)_2$ and $Bi_3(GaO_4)(MoO_4)_2$-new compounds with Scheelite related structures, Mater. Res. Bull. 9 (1974) 951–954.
[18] U. Kolitsch, E. Tillmanns, $Bi_3ScMo_2O_{12}$: the difference from Bi_3Fe-Mo_2O_{12}, Acta Crystallogr. E 59 (2003) I43–I46.
[19] D.D. Khalyavin, A.M.R. Senos, P.Q. Mantas, D.N. Argyriou, I.T. Gomes, L.G. Vieira, J.L. Ribeiro, Structure and dielectric characterization of a new A-site deficient $La_{5/3}MgTaO_6$ perovskite, J. Solid State Chem. 180 (2007) 41–48.