Journal of Alloys and Compounds 781 (2019) 385–388

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Temperature independent low firing $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ($0.2 \leq x \leq 0.8$) microwave dielectric ceramics

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

[a] Micro-optoelectronic Systems Laboratories, 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

ARTICLE INFO

Article history:
Received 16 October 2018
Received in revised form
7 December 2018
Accepted 8 December 2018
Available online 10 December 2018

Keywords:
Scheelite
Microwave dielectric properties
MoO_3
Low temperature sintering

ABSTRACT

A scheelite structured $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ($0.2 \leq x \leq 0.8$) ceramics were prepared via solid state reaction method. All the ceramics can be well densified below 780 °C. As x value increased from 0.2 to 0.8, microwave dielectric permittivity increased from 14.0 to 27.8, Qf (Q = quality factor = 1/dielectric loss; f = resonant frequency) value decreased from 42,000 GHz to 19,000 GHz, and TCF shifted from −50 ppm/°C to +18 ppm/°C. The best microwave dielectric properties with permittivity between 23.54 and 23.56, Qf value between 24,000 GHz–21,000 GHz and TCF value ~ −8 ppm/°C in wide temperature range 25 °C–130 °C were obtained in x = 0.6 ceramic. This work showed that Bi played an important role to modify the TCF from negative to positive value in scheelite materials and this result further accelerate the application of scheelite materials in low temperature co-fired ceramics (LTCC) technology.

1. Introduction

Microwave dielectric ceramics have played important roles in dielectric resonator, filter and substrate. Search for novel materials with high quality factor Q (low dielectric loss), low sintering temperature with co-sinterable metal electrode are current two hot topics microwave dielectric ceramics due to the fast development of low temperature co-fired ceramics (LTCC) technology, which is a very popular fabrication method in modern electronic devices [1–6]. Most commercial microwave dielectric ceramics with high Qf value (Q = 1/dielectric loss; f = resonant frequency) belong to the famous ABO_3 perovskite structure [7–9]. However, it is quite difficult to lower the sintering temperatures of ABO_3 perovskite ceramics to below the melting point (961 °C) of most common metal electrode silver in LTCC technology without serious deterioration in Qf values. Recently, another large family called scheelite has attracted much attention due to the adaptability of this structure, high Qf value and adjustable temperature coefficient of resonant frequency (TCF) value [10–13]. Hong et al. [10,11] first reported the microwave dielectric properties of AWO_4 and $AMoO_4$ (A = Ca, Sr, Ba) ceramics and they show low permittivity (8–17), high Qf values (32,000–69,000 GHz), and negative TCF values (−53 to −78 ppm/°C). Although this system possesses high Qf value, their TCF value are all large negative. Subsequently, another alkali metal bismuth molybdates system $(ABi)_{1/2}MoO_4$ (A = Li, Na, K, Rb, Ag) with scheelite and scheelite related structures were also reported to possess good microwave dielectric properties and some of them show positive TCF value [14–16]. Among them, $(LiBi)_{1/2}MoO_4$ possesses an ultralow sintering temperature ~ 560 °C, the largest permittivity ~ 41.7 (at 5.5 GHz), the largest positive TCF value ~+ 240 ppm/°C but a poor Qf value ~3200 GHz [14]. The $(LiBi)_{1/2}MoO_4$ was found to form solid solution with $CaMoO_4$ in the full composition range and near zero TCF value was achieved in the $[(Li_{0.5}Bi_{0.5})_{0.15}Ca_{0.85}]MoO_4$ ceramic with a relative permittivity ~ 14.1, a Qf value ~ 24,000 GHz (at 10.0 GHz) [17]. Except for $(LiBi)_{1/2}MoO_4$, $(NaBi)_{1/2}MoO_4$ and $(AgBi)_{1/2}MoO_4$ are the only two scheelite compounds that have been reported to possess positive TCF value by now [15]. The $(NaBi)_{1/2}MoO_4$ was also used to compensate the TCF value of $CaMoO_4$ ceramic and a temperature stable $(Na_{0.5}Bi_{0.5})_{0.6}Ca_{0.4}MoO_4$ microwave ceramic with a permittivity ~ 21.9 and a Qf value ~ 20,660 GHz was achieved [18]. Compared with both $(LiBi)_{1/2}MoO_4$ and $(AgBi)_{1/2}MoO_4$, $(NaBi)_{1/2}MoO_4$ possesses higher Qf value and low cost ingredients, and

* Corresponding author.
E-mail address: zhoudi1220@gmail.com (D. Zhou).

https://doi.org/10.1016/j.jallcom.2018.12.125
0925-8388/

worked well to compensate negative TCF in many other scheelite phases, such as $(Na_{0.5}La_{0.5})MoO_4$ and $(Na_{0.5}Bi_{0.5})WO_4$ etc. [19,20] As well know, scheelite structure is quite adaptable and as large as 1/3 defect can be allowed on the A site as reported in $(\Phi_{1/3}La_{2/3})MoO_4$ ceramic [21–23]. In our previous work, it was also found that A site defect can be used to modify the TCF values [24,25]. Besides, heavy Bi^{3+} was found to accelerate shifting TCF value from negative to positive in many systems [26,27]. Hence, in the present work, the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ $(0.2 \le x \le 0.8)$ ceramics were prepared via solid state reaction method. The sintering behavior and microwave dielectric properties were studied in detail.

2. Experimental section

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), $CaCO_3$, Nd_2O_3 (>99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were measured according to the stoichiometric formulation $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ $(0.2 \le x \le 0.8)$. Ceramic samples were prepared via the traditional solid state reaction method as described in our previous work [2,15]. The calcination temperature is 600 °C and the samples were sintered under air atmosphere in 660–780 °C. Room temperature X-ray diffraction (XRD) was performed using a XRD with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Prior to examination sintered pellets were crushed in a mortar and pestle to powder. Diffraction pattern was obtained between 2θ of 5–65° for phase identification at a step size of 0.02°. Dielectric properties at microwave frequency were measured with 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). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

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

where the f_T and f_{T0} were the $TE_{01\delta}$ resonant frequencies at temperature T and T_0, respectively.

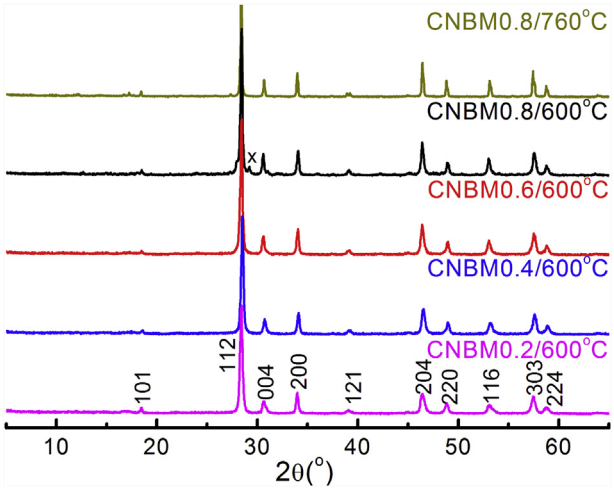

Fig. 1. XRD patterns of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics calcined at 600 °C and sintered at 760 °C for x = 0.2.

3. Results and discussions

XRD patterns of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics calcined at 600 °C and sintered at 760 °C for x = 0.2 are shown in Fig. 1. Single scheelite phases were formed in almost all the compositions except for x = 0.8 after calcinations at 600 °C. The intensity of XRD of secondary phases in x = 0.8 sample are quite weak and it might be Nd_2MoO_6 or $Bi_2Mo_3O_{12}$ or both. After being well sintered at 680 °C, the secondary phases disappeared and pure scheelite phase was formed. Although 25 mol. % defects were introduced on the A site, scheelite phase can also be kept in the full composition range here and it is very adaptable.

Microwave dielectric permittivity and Qf value of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics as a function of sintering temperature are shown in Fig. 2. As sintering temperature increased, permittivity of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ceramics increased first and then reached their separate saturated values. Qf values also showed similar trend and also good stability in wide sintering temperature ranges. As the x value increased from 0.2 to 0.8, sintering temperature decreased gradually from 780 °C to 680 °C due to the increase in Bi content (melting points of Bi_2O_3 is 817 °C << 2233 °C for Nd_2O_3). Meanwhile, microwave permittivity increased from about 14 to 27.8 and Qf value decreased from 42,000 GHz to 19,000 GHz and this might be attributed to the larger ionic polarizability of Bi^{3+} (6.12 Å^3) than that of Nd^{3+} (5.01 Å^3) as reported by Shannon [28]. Dielectric polarizations at microwave region are commonly contributed from the ionic and electronic displacive polarizations, in which the latter's contribution can be ignored in high k materials. A classic damped oscillator model can be employed to describe the relative displacement of cations and anions, from which an inversely proportional relation between the Qf and εr can be deduced as the following [17,29].

$$Q \times f \approx \frac{(ze)^2 / mV\varepsilon_0}{2\pi\gamma \times (\varepsilon'(\omega) - \varepsilon(\infty))} \quad (2)$$

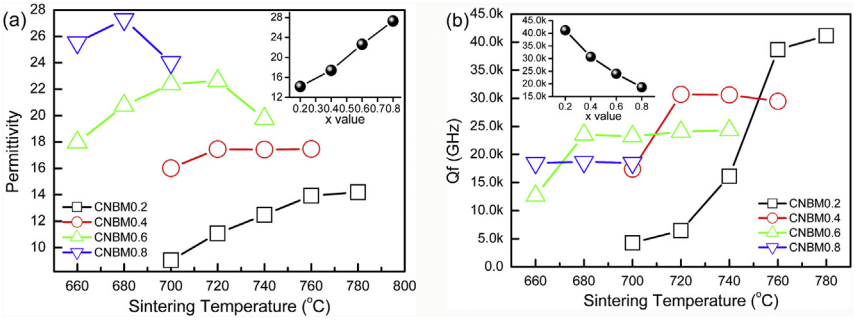

Fig. 2. Microwave dielectric permittivity (a) and Qf value of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics as a function of sintering temperature.

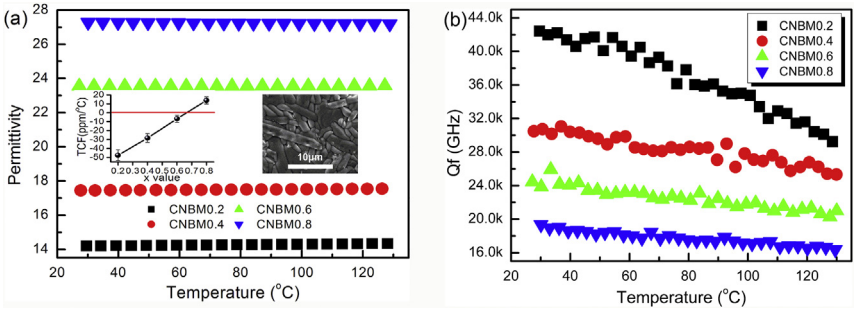

Fig. 3. Temperature dependence of microwave dielectric permittivity (a) and Qf value (b) of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics (inset is the thermal etched surface of x = 0.6 sample sintered at 720 °C).

This relation can well explain the relation between x value, permittivity and Qf values of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ solid solution system.

Temperature dependence of microwave dielectric permittivity, Qf value and the TCF values of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics are shown in Fig. 3. As shown in the inset of Fig. 3a, TCF values shifted linearly from −50 ppm/°C for x = 0.2 sample to +18 ppm/°C for x = 0.8 sample. TCF value gives the temperature dependence of resonant frequency and it is mainly determined by the temperature dependence of permittivity. As shown in Fig. 3a, permittivity of the x = 0.6 sample increased slightly from 23.54 to 23.56 as temperature changed from 25 °C to 130 °C and shows quite good temperature independency. Different from the large drop in Qf value for x = 0.2 sample as temperature increased, the Qf value of x = 0.6 ceramic decreased slightly from 24,000 GHz at 25 °C to 21,000 GHz at 130 °C, which means this ceramic is quite isolating and shows quite low dielectric loss in wide temperature range. Also, the x = 0.6 ceramic sintered at 720 °C shows quite dense microstructure as seen from the inset in Fig. 3a, which indicates that Bi substation for Nd remarkably lowered the densification temperatures of the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ceramics.

4. Conclusions

A scheelite solid solution with 25 mol. % defect on A site was formed in the $[Ca_{0.25}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.4, 0.6 and 0.8) ceramics. All the ceramics can be well densified below 780 °C. As the increase of Bi content in this system, TCF value can be easily modified from negative to positive values. Temperature stable microwave dielectric properties can be obtained in x = 0.6 sample with permittivity about 23.54–23.56 and Qf value between 24,000 GHz–21,000 GHz in wide temperature range 25 °C–130 °C and this system might be good candidate for LTCC technology.

Declarations of interest

None.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (Grant No. 2017YFB0406301), the Young Star Project of Science and Technology of Shaanxi Province (2015KJXX-39), the Fundamental Research Funds for the Central University, and the State Key Laboratory of New Ceramic and Fine Processing Tsinghua University.

References

[1] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, Int. Mater. Rev. 53 (2008) 57–90.
[2] H. Zhou, X. Tan, X. Chen, H. Ruan, Effect of raw materials pretreated by physical grinding method on the sintering ability and microwave dielectric properties of Li_2MgTiO_4 ceramics, J. Alloys Compd. 731 (2018) 839–843.
[3] I.M. Reaney, D. Iddles, Microwave dielectric ceramics for resonators and filters in mobile phone networks, J. Am. Ceram. Soc. 89 (2006) 2063–2072.
[4] 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 co-fired ceramic architecture, J. Mater. Chem. C 5 (2017) 10094–10098.
[5] H. Zhou, X. Tan, J. Huang, N. Wang, G. Fan, X. Chen, Phase structure, sintering behavior and adjustable microwave dielectric properties of $Mg_{1-x}Li_{2x}Ti_xO_{1+2x}$ solid solution ceramics, J. Alloys Compd. 696 (2017) 1255–1259.
[6] L.X. Pang, D. Zhou, Z.M. Qi, W.G. Liu, Z.X. Yue, I.M. Reaney, Structure–property relationships of low sintering temperature scheelite-structured (1-x) $BiVO_4$–x$LaNbO_4$ microwave dielectric ceramics, J. Mater. Chem. C 5 (2017) 2695–2701.
[7] S. Kawashima, M. Nishida, I. Ueda, H. Ouchi, $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with low dielectric loss at microwave frequencies, J. Am. Ceram. Soc. 66 (1983) 421–423.
[8] R.I. Scott, M. Thomas, C. Hampson, Development of low cost, high performance $Ba(Zn_{1/3}Nb_{2/3}O_3)$ based materials for microwave resonator applications, J. Eur. Ceram. Soc. 23 (2003) 2467–2471.
[9] B. Jancar, D. Suvorov, M. Valant, G. Drazic, Characterization of $CaTiO_3$-$NdAlO_3$ dielectric ceramic, J. Eur. Ceram. Soc. 23 (2003) 1391–1400.
[10] 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.
[11] 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.
[12] 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.
[13] E.S. Kim, S.H. Kim, B.I. Lee, Low-temperature sintering and microwave dielectric properties of $CaWO_4$ ceramics for LTCC applications, J. Eur. Ceram. Soc. 26 (2006) 2101–2104.
[14] D. Zhou, C.A. Randall, H. Wang, L.X. Pang, X. Yao, Microwave dielectric ceramics in Li_2O-Bi_2O_3-MoO_3 system with ultra low sintering temperatures, J. Am. Ceram. Soc. 93 (2010) 1096–1100.
[15] D. Zhou, C.A. Randall, L.X. Pang, H. Wang, J. Guo, G.Q. Zhang, Y. Wu, K.T. Guo, L. Shui, X. Yao, Microwave dielectric properties of $(ABi)_{1/2}MoO_4$ (A = Li, Na, K, Rb, Ag) type ceramics with ultra-low firing temperatures, Mater. Chem. Phys. 129 (2011) 688–692.
[16] L.X. Pang, D. Zhou, J. Guo, Z.X. Yue, X. Yao, Microwave dielectric properties of $(Li_{0.5}Ln_{0.5})MoO_4$ (Ln = Nd, Er, Gd, Y, Yb, Sm, and Ce) ceramics, J. Am. Ceram. Soc. 98 (2015) 130–135.
[17] D. Zhou, H. Wang, Q.P. Wang, X.G. Wu, J. Guo, G.Q. Zhang, L. Shui, X. Yao, C.A. Randall, L.X. Pang, H.C. Liu, Microwave dielectric properties and Raman spectroscopy of scheelite solid solution $[(Li_{0.5}Bi_{0.5})_{1-x}Ca_x]MoO_4$ ceramics with ultra-low sintering temperatures, Funct. Mater. Lett. 3 (2010) 253–257.
[18] J. Guo, D. Zhou, Y. Li, T. Shao, Z.M. Qi, B.B. Jin, H. Wang, Structure–property relationships of novel microwave dielectric ceramics with low sintering temperatures: $(Na_{0.5x}Bi_{0.5x}Ca_{1-x})MoO_4$, Dalton Trans. 43 (2014) 11888–11896.
[19] W.B. Li, D. Zhou, H.H. Xi, L.X. Pang, X. Yao, Structure, infrared reflectivity and microwave dielectric properties of $(Na_{0.5}La_{0.5})MoO_4$–$(Na_{0.5}Bi_{0.5})MoO_4$ ceramics, J. Am. Ceram. Soc. 99 (2016) 2083–2088.
[20] L.X. Pang, D. Zhou, Z.M. Qi, Z.X. Yue, Influence of W substitution on crystal structure, phase evolution and microwave dielectric properties of $(Na_{0.5}Bi_{0.5})MoO_4$ ceramics with low sintering temperature, Sci. Rep. 7 (2017) 3201.
[21] A.W. Sleight, W.J. Linn, Olefin oxidation over oxide catalysts with the scheelite

structure, Ann. N. Y. Acad. Sci. 272 (1976) 22–44.
[22] L.H. Brixner, A.W. Sleight, M.S. Licis, Cell dimensions of the molybdates $La_2(MoO_4)_3$, $Ce_2(MoO_4)_3$, $Pr_2(MoO_4)_3$, and $Nd_2(MoO_4)_3$, J. Solid State Chem. 5 (1972) 247–249.
[23] W. Jeitschko, Crystal structure of $La_2(MoO_4)_3$, a new ordered defect Scheelite type, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 29 (1973) 2074–2081.
[24] J. Guo, C.A. Randall, G.Q. Zhang, D. Zhou, Y.Y. Chen, H. Wang, Synthesis, structure, and characterization of new low-firing microwave dielectric ceramics: $(Ca_{1-3x}Bi_{2x}\Phi_x)MoO_4$, J. Mater. Chem. C 2 (2014) 7364–7372.
[25] D. Zhou, W.B. Li, L.X. Pang, J. Guo, Z.M. Qi, T. Shao, X. Yao, C.A. Randall, Phase evolution and microwave dielectric properties of $xBi_{2/3}MoO_4$-(1-x)$BiVO_4$ ($0.0 \leq x \leq 1.0$) low temperature firing ceramics, Dalton Trans. 43 (2014) 7290–7297.
[26] 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.
[27] D. Zhou, J. Li, L.X. Pang, G.H. Chen, Z.M. Qi, D.W. Wang, I.M. Reaney, Crystal structure, infrared spectra, and microwave dielectric properties of temperature-stable zircon-Type (Y,Bi)VO_4 solid-Solution ceramics, ACS Omega 1 (2016) 963–970.
[28] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.
[29] J. Petzelt, S. Kamba, Submillimetre and infrared response of microwave materials: extrapolation to microwave properties, Mater. Chem. Phys. 79 (2003) 175–180.