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Microwave dielectric properties of $BaY_2(MoO_4)_4$ ceramic with low sintering temperature

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Abstract A low firing microwave dielectric ceramic $BaY_2(MoO_4)_4$ with monoclinic phase was prepared by using solid state reaction method. Microstructure and microwave dielectric properties of the ceramic were investigated. Optimized microwave dielectric properties were obtained in the ceramic sintered at 925 °C for 2 h with a relative permittivity ~11.5, a Q × f value about 47,200 GHz (at 10.3 GHz) and a temperature coefficient of resonant frequency of −35 ppm/°C. Furthermore, $0.5BaY_2(MoO_4)_4$–$0.5TiO_2$ ceramic sintered at 970 °C for 2 h with a relative permittivity ~13.6, a Q × f value about 30,800 GHz (at 9.6 GHz) and a near zero τ_f value of +0.8 ppm/°C.

1 Introduction

With the rapid development of microwave communication technologies, multilayer microwave devices have been widely used in microwave circuit miniaturization and integration. As an efficient method to fabricate multilayer microwave devices, low-temperature co-fired ceramic (LTCC) technology has been intensively investigated over past decades for circuit miniaturization and integration. LTCC requires microwave dielectric ceramics with high performance and low sintering temperature. Microwave dielectric ceramics with derived dielectric permittivities ε_r, high Q × f, low temperature coefficient of resonant frequency τ_f and nontoxic constituents are more and more important [1–7].

$MR_2(MoO_4)_4$ (M: bivalent alkaline earth metal ion and R: trivalent rare earth ion) compounds are well known as optical materials and belong to a group of double alkaline earth lanthanide molybdates. Due to their spectroscopic characteristics, $MR_2(MoO_4)_4$ compounds have been paid much attention as new laser crystal materials [8–12]. Recent studies indicated that many MoO_3-rich systems possess high microwave dielectric properties [13–16]. Microwave dielectric properties of a new class of $BaCe_2(MoO_4)_4$ ceramics with ε_r ~12.3, Q × f ~16,000–24,000 GHz and τ_f ~ −37 ppm/ °C were reported for the first time by James et al. [17, 18]. Subsequently, the effect of ionic radii of lanthanides such as La, Nd and Sm on microwave dielectric properties of $BaLn_2(MoO_4)_4$ ceramics with a ε_r ~10.3–11.7, Q × f ~20,000–45,000 GHz and τ_f ~ −76 to −45 ppm/°C was reported [19, 20].

In this work, a MoO_3-rich $BaY_2(MoO_4)_4$ ceramic was prepared by using solid state reaction method. Microstructure, microwave dielectric properties and properties for temperature compensation with TiO_2 were studied.

2 Experimental procedure

Proportionate amounts of reagent-grade $BaCO_3$ (99 %, Guo-Yao Co. Ltd., Shanghai, China), Y_2O_3 (99.99 %, Guo-Yao Co, Ltd, Shanghai, China), MoO_3 (99.95 %, Yutong Chemical Reagents, Tianjin, China) and TiO_2 (99.85 %, Linghua Co. Ltd., Zhaoqing, China) were weighted according to the stoichiometric compositions of $BaY_2(MoO_4)_4$. Y_2O_3 powders were calcined at 800 °C for 4 h before weighting. The mixed powders were milled in absolute ethyl alcohol with zirconia balls (2 mm in

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diameter) as milling media using polyethylene jars and planetary mill (QM-1F; Nanjing Machine Factory, Nanjing, China) for 4 h at a running speed of 150 rpm, which were then calcined in air at 800 °C for 4 h. After being crushed, they were re-milled for 5 h at 200 rpm to increase reactivity and homogeneity. Then, the dried powders granulated with 5 wt% polyvinyl alcohol (PVA) were uniaxially pressed into cylinders (12 mm in diameter and 5 mm in height) in a steel die under pressure of 150 MPa. PVA was burnt out at 550 °C for 5 h (2 °C/min). Samples were sintered in the temperature ranges from 900 to 970 °C for 2 h.

The crystalline structures of samples were investigated by using X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of the sintered ceramic were characterized with scanning electron microscopy (SEM) (SEM; Quanta 250 F, FEI). Bulk densities of the sintered ceramics were measured by using Archimedes' method. Microwave dielectric behaviors were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25–85 °C. Temperature coefficient of resonant frequency (TCF or τ_f value) was calculated with the following formula:

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

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3 Results and discussion

XRD patterns of the $BaY_2(MoO_4)_4$ powder calcined at 800 °C and ceramic samples sintered at different temperatures are shown in Fig. 1. Pure monoclinic $BaY_2(MoO_4)_4$ phase was observed at 875–950 °C [18, 20]. The $BaY_2(MoO_4)_4$ ceramics had a monoclinic structure with cell parameters a = 4.061, b = 15.658 and c = 9.973 Å. Detailed crystal structure analysis of $BaY_2(MoO_4)_4$ compositions has not been reported so far.

Surface SEM micrographs of the $BaY_2(MoO_4)_4$ ceramic sintered at 875–975 °C for 2 h are shown in Fig. 2. Porosity of the $BaY_2(MoO_4)_4$ ceramics decreased with increasing sintering temperature and reaching maximum density at 925 °C. Grain size of the $BaY_2(MoO_4)_4$ ceramics increased with increasing sintering temperature.

Bulk density and permittivity ε_r of the $BaY_2(MoO_4)_4$ ceramic as a function of sintering temperature are shown in

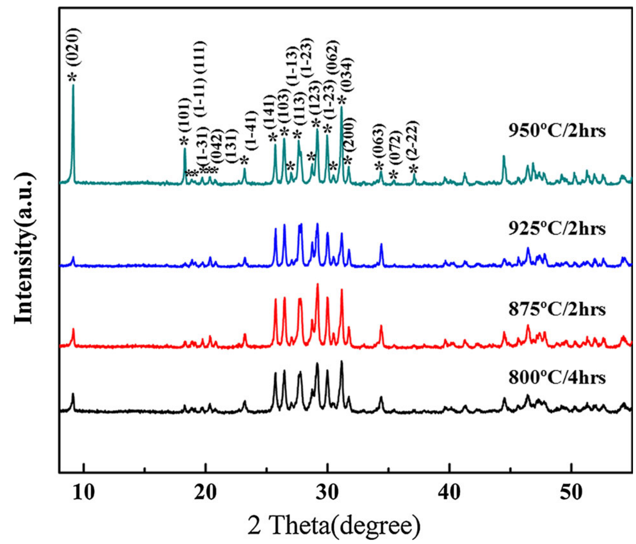

Fig. 1 The XRD patterns of $BaY_2(MoO_4)_4$ ceramics samples sintered at various temperatures for 2 h in air: **a** 800 °C, **b** 875 °C, **c** 925 °C, and **d** 950 °C

Fig. 3. As the sintering temperature was increased from 875 to 925 °C, bulk density of the $BaY_2(MoO_4)_4$ ceramic increased from 4.599 to 4.787 g/cm^3 and reached maximum value. Then, the density began to decrease from 4.787 to 4.726 g/cm^3, as the sintering temperature was increased from 925 to 975 °C. The bulk density results were in good agreement with the SEM observation. The variation in ε_r value is similar to that of bulk density. As the sintering temperature was up to 950 °C, ε_r reached the maximum value of 11.7.

$Q \times f$ and τ_f values of the $BaY_2(MoO_4)_4$ ceramics sintered at 875–975 °C for 2 h in air are shown in Fig. 4. With increasing sintering temperature, the $Q \times f$ value increases to a maximum value of 47,200 GHz ($f = 10.3$ GHz) at 925 °C. With further increase in sintering temperature, the $Q \times f$ value decreases to 38,000 GHz ($f = 10.2$ GHz) at 975 °C, which might result from the secondary grain growth. No significant variation in τ_f value for the $BaY_2(MoO_4)_4$ ceramic was observed, while the τ_f value was ranged from −30 ppm/°C (at 875 °C) to −32.6 ppm/°C (at 975 °C). Best microwave dielectric properties were obtained in $BaY_2(MoO_4)_4$ ceramic sample sintered at 925 °C for 2 h with a permittivity ~11.5, a Q × f value of 47,200 GHz and a temperature coefficient of −35 ppm/°C. However, the $BaY_2(MoO_4)_4$ ceramic with large negative TCF values restricts its applications in microwave devices. Rutile TiO_2 has a large permittivity (~105), a high Q × f value (~46,000 GHz) and a large positive TCF value (~ +400 ppm/°C), so it can be a good candidate to tailor the properties of the $BaY_2(MoO_4)_4$. Table 1 shows the

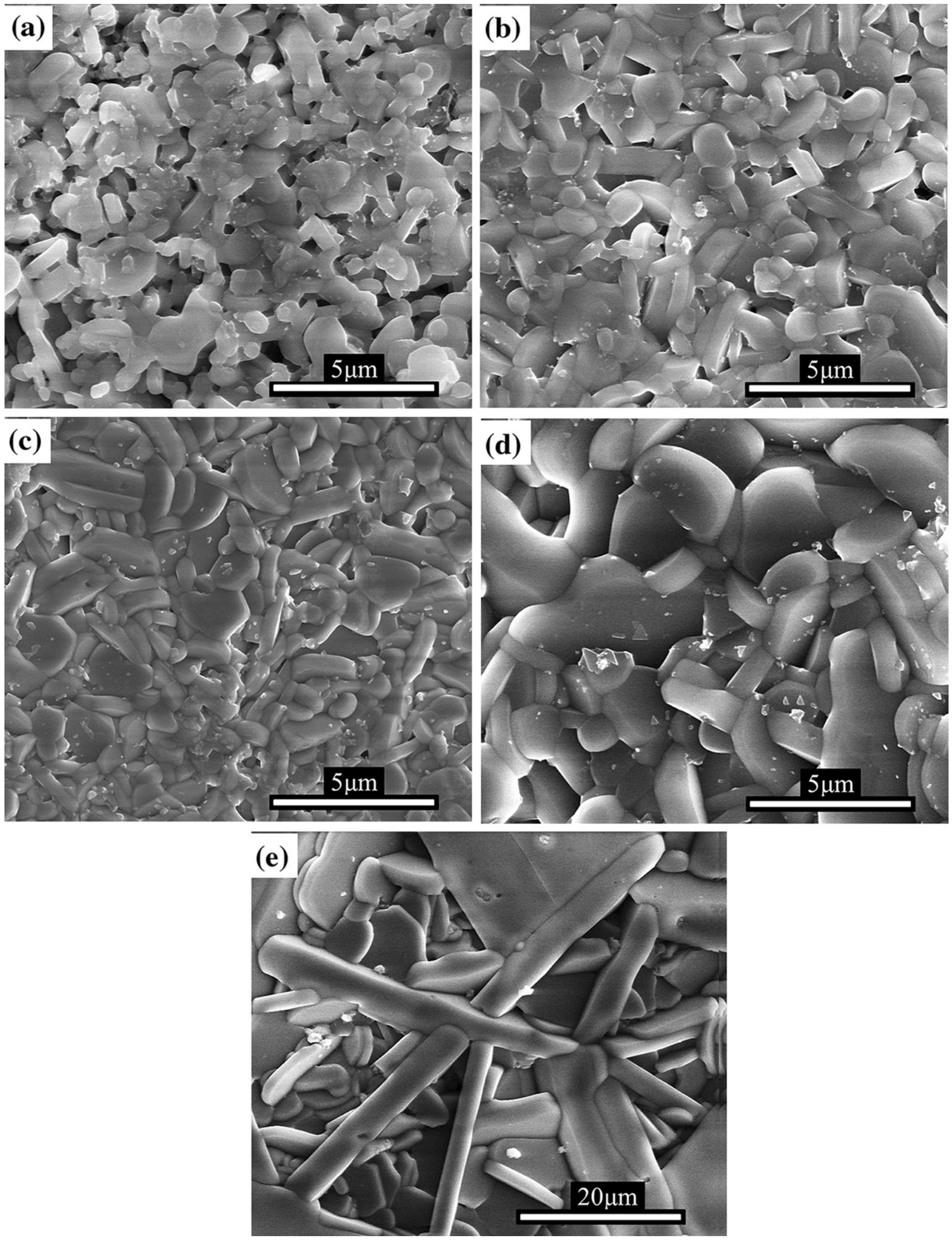

Fig. 2 The SEM micrograph of $BaY_2(MoO_4)_4$ ceramic sintered at various temperatures: **a** 875 °C, **b** 900 °C, **c** 925 °C, **d** 950 °C, and **e** 975 °C for 2 h

microwave dielectric properties of the temperature stable ceramics $(1-x)BaY_2(MoO_4)_4$–$xTiO_2$($x = 0.45$–0.55) sintered at optimized sintering temperature. The $0.50BaY_2(MoO_4)_4$–$0.50TiO_2$ ceramic can be sintered at 970 °C, with a near zero τ_f value of 0.8 ppm/ °C, a permittivity of 13.6 and a Q × f value of 30,800 GHz.

4 Conclusions

$BaY_2(MoO_4)_4$ ceramic possessed good microwave dielectric properties and low sintering temperatures. High performance microwave dielectric properties were obtained in the sample sintered at 925 °C for 2 h, with microwave

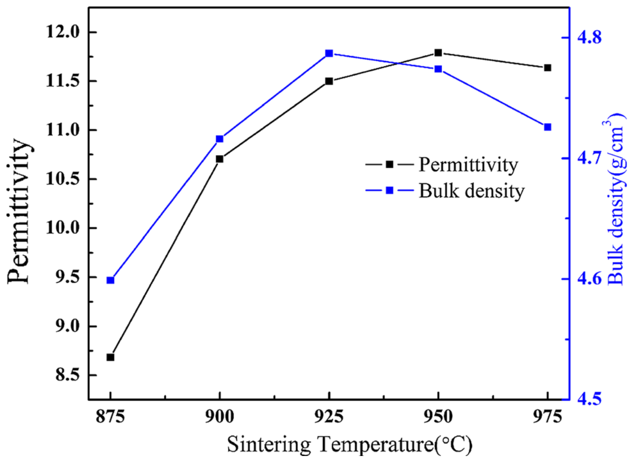

Fig. 3 Bulk densities and permittivity of $BaY_2(MoO_4)_4$ ceramics as a function of sintering temperatures

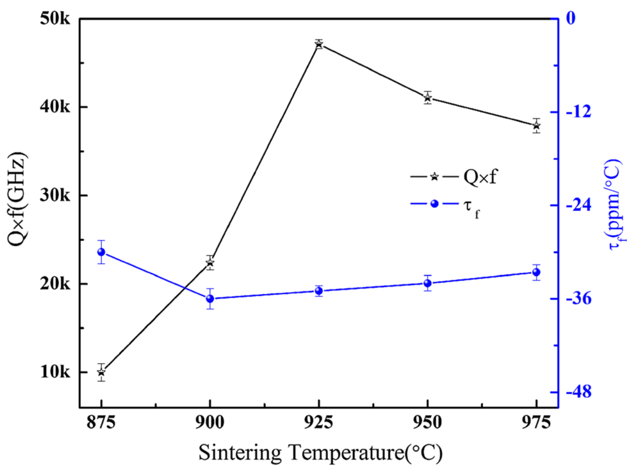

Fig. 4 Microwave dielectric properties (Q × f value, TCF) of $BaY_2(MoO_4)_4$ ceramics as a function of sintering temperatures

Table 1 Microwave dielectric properties of $(1-x)BaY_2(MoO_4)_4$–$xTiO_2$ ceramics

Composition	ST (°C)	Permittivity	Qf (GHz)	TCF (ppm/°C)
$BaY_2(MoO_4)_4$	925	11.5	45,000	−35
$0.55BaY_2(MoO_4)_4$–$0.45TiO_2$	950	12.4	32,400	−3.3
$0.50BaY_2(MoO_4)_4$–$0.50TiO_2$	970	13.6	30,800	+0.8
$0.45BaY2(MoO_4)_4$–$0.55TiO_2$	970	14.2	30,300	+1.7

ST sintering temperature, *TCF* temperature coefficient of resonant frequency

permittivity of ∼11.5,Q × f of ∼47,200 GHz and temperature coefficient of ∼ −35 ppm/°C. Furthermore, $0.5BaY_2(MoO_4)_4$–$0.5TiO_2$ ceramic sintered at 970 °C for 2 h with a relative permittivity of ∼13.6, a Q × f value of about 30,800 GHz (at 9.6 GHz) and a near zero τ_f value of +0.8 ppm/°C.

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References

1. M.T. Sebastian, Int. Mater. Rev. **53**, 57–90 (2008)
2. M.A. Rodriguez, P. Yang, P. Kotula, D. Dimos, J. Electroceram. **5**, 217 (2000)
3. Y. Wu, D. Zhou, J. Guo, L.X. Pang, J. Mater. Sci. Mater. Electr. **24**, 1505 (2013)
4. C.L. Huang, W.R. Yang, P.C. Yu, J. Eur. Ceram. Soc. **34**, 277–284 (2014)
5. D. Thomas, P. Abhilash, M.T. Sebastian, J. Eur. Ceram. Soc. **33**, 87–93 (2013)
6. O.A. Shlyakhtin, Y.J. Oh, J. Am. Ceram. Soc. **89**, 3366–3372 (2006)
7. D. Zhou, H. Wang, L.X. Pang, C.A. Randall, X. Yao, J. Am. Ceram. Soc. **92**, 2242–2246 (2009)
8. C. Cascales, A. Méndez-Blas, M. Rico, V. Volkov, C. Zaldo, Opt. Mater. **27**, 1672–1680 (2005)
9. L. Qin, Y.L. Huang, T. Tsuboi, H.J. Seo, Mater. Res. Bull. **47**, 4498–4502 (2012)
10. C.F. Guo, H.K. Yang, J.H. Jeong, J. Lumin. **130**, 1390–1393 (2010)
11. Y.H. Zheng, X.X. Lin, Q.M. Wang, W.S. Cai, C.C. Zhang, Mater. Res. Bull. **47**, 856–860 (2012)
12. S.J. Han, J.Y. Wang, J. Li, Y.J. Guo, Y.Z. Wang, L.L. Zhao, J. Lumin. **131**, 244–246 (2011)
13. L.X. Pang, D. Zhou, W.G. Liu, J. Am. Ceram. Soc. **97**, 2032–2034 (2014)
14. G.K. Choi, S.Y. Cho, J.S. An, K.S. Hong, J. Eur. Ceram. Soc. **26**, 2011–2015 (2006)
15. G.K. Choi, J.R. Kim, S.H. Yoon, K.S. Hong, J. Eur. Ceram. Soc. **27**, 3063–3067 (2007)
16. L.X. Pang, G.B. Sun, D. Zhou, Mater. Lett. **65**, 164–166 (2011)
17. N.K. James, R. Ratheesh, J. Am. Ceram. Soc. **93**, 931–933 (2010)
18. A. Surjith, R. Ratheesh, J. Alloy. Compd. **550**, 169–172 (2013)
19. D. Zhou, L.X. Pang, J. Guo, Y. Wu, G.Q. Zhang, W. Dai et al., J. Am. Ceram. Soc. **94**, 2800–2803 (2011)
20. L.X. Pang, H. Liu, D. Zhou, G.B. Sun, W.G. Qin, W.G. Liu, Mater. Lett. **72**, 128–130 (2012)