Materials Letters 162 (2016) 91–93

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A novel microwave dielectric ceramic of $BaMgP_2O_7$ with low ε_r

Huidong Xie*, Chao Chen, Ran Tian, Haihong Xi

School of Science, Xi'an University of Architecture and Technology, Xi'an 710055, PR China

ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form
7 September 2015
Accepted 30 September 2015
Available online 3 October 2015

Keywords:
Ceramics
Dielectrics
Pyrophosphate

ABSTRACT

A novel microwave dielectric ceramic of $BaMgP_2O_7$ with low dielectric constant and high quality factor was synthesized by the solid-state reaction method. Dense ceramic with 96.8% relative density was obtained when the ceramic sintered at 850 °C for 2 h. The $BaMgP_2O_7$ ceramic sintered at 850 °C for 2 h possessed good microwave dielectric properties: ε_r=6.8, $Q \times f$=40,089 GHz (at 11.7 GHz), and τ_f=−40.6 ppm/°C.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The rapid development of the wireless communication industry has created the high demand for the development of microwave components. Advanced substrate materials for microwave integrated circuits require a low dielectric constant ($\varepsilon_r < 10$) to maximize the signal propagation speed, a high quality factor ($Q \times f$) to increase the frequency selectivity, and a near-zero temperature coefficient of resonance frequency (τ_f) to ensure the stability of the frequency against temperature changes [1–4]. At present, many low ε_r ceramics such as Al_2O_3, AO–SiO_2 (A=Ca, Mg, Zn), $MTiO_3$ (M=Mg, Ca) have good microwave dielectric properties but high sintering temperatures, which is energy-consuming. Therefore, the study of microwave dielectric ceramics with low sintering temperature is necessary [5–7]. Pyrophosphates are stable crystalline compounds and have been reported to possess good microwave dielectric properties as well as relatively low sintering temperature [8–11]. For example, $SrZnP_2O_7$ ceramics sintered at 940 °C have the properties of ε_r=7.02, $Q \times f$=23,000 GHz, and τ_f=−84.7 ppm/°C [12]. $CaZnP_2O_7$ ceramics sintered at 900 °C exhibit good dielectric properties of ε_r=7.56, $Q \times f$=63,130, τ_f=−82 ppm/°C [13]. In 1995, the crystal structure of $BaMgP_2O_7$ was reported. After then luminescence of $BaMgP_2O_7:Eu^{2+}$, Mn^{2+} and $BaMgP_2O_7:Eu^{3+}$ and infrared spectra of $BaMgP_2O_7$ were reported by Kim [14], Wang [15] and Idrissi [16] et al. To date there are no reports on the microwave dielectric properties of $BaMgP_2O_7$. In the present work, the $BaMgP_2O_7$ ceramic was prepared via the solid state reaction method. The sintering behavior, microstructure, microwave dielectric properties were studied in detail.

2. Experimental

$BaMgP_2O_7$ powders were synthesized by the solid-state reaction route using analytical grade powders of $BaCO_3$, $NH_4H_2PO_4$, and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$. Stoichiometric starting materials were weighed, mixed and grounded for 2 h using anhydrous ethanol as grinding media in an agate mortar. Then the powders were dried at 80 °C for 12 h, and calcined at 800 °C for 4 h in an alumina crucible. The as-calcined powders were dried, mixed with 5 wt% PVA binder, granulated, and pressed into cylinders (12 mm in diameter and 3 mm in height) under a uniaxial pressure of 10 MPa. Ceramics of $BaMgP_2O_7$ were sintered in air atmosphere at 825–925 °C for 2 h. Powder X-ray diffraction (XRD) patterns were taken at room temperature by using a Bruker D8 Advance diffractometer with Cu Kα radiation. The microstructure of the ceramics on the surface was evaluated by field scanning electron microscopy (SEM) (Quanta 600 FEG, FEI) at an accelerating volt of 20 keV. The bulk densities of sintered pellets were measured by the Archimedes' method. Microwave dielectric behaviors at microwave frequency 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. The temperature coefficient of resonant frequency τ_f value (ppm/°C) was calculated using the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \text{ppm/}^{o}\text{C}$$

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

* Corresponding author. Fax: +86 29 82202335.
E-mail address: xiehuidong@tsinghua.org.cn (H. Xie).

http://dx.doi.org/10.1016/j.matlet.2015.09.131
0167-577X/© 2015 Elsevier B.V. All rights reserved.

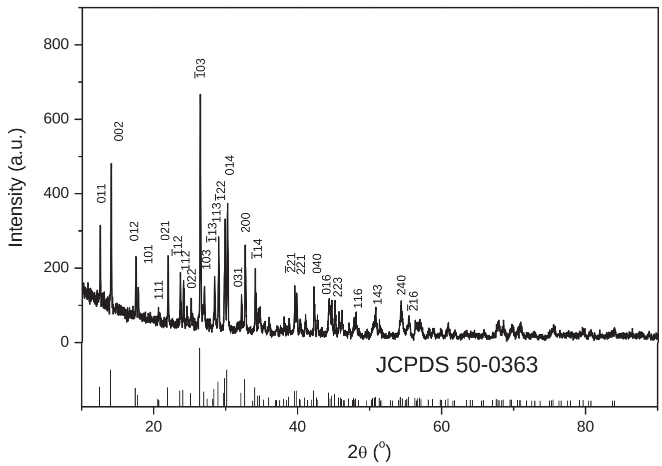

Fig. 1. XRD patterns of $BaMgP_2O_7$ powders calcined at 800 °C for 4 h in air.

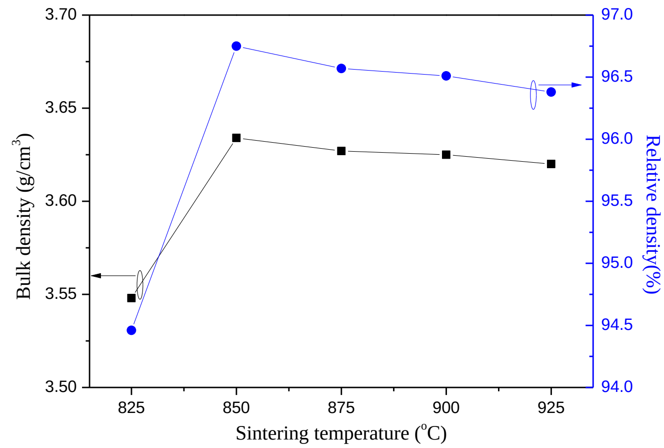

Fig. 3. Varition of bulk density and relative density with sintering temperature of $BaMgP_2O_7$ ceramic.

3. Results and discussion

Fig. 1 showed the XRD patterns of $BaMgP_2O_7$ powders calcined at 800 °C for 4 h. All the peaks in the X-ray diffraction patterns can be indexed based on the JCPDS no. 50–0363 of $BaMgP_2O_7$. No additional peaks were found in the patterns, indicating that there were no other impurity phases in the powders. The XRD results showed the $BaMgP_2O_7$ powders calcined at 800 °C crystallized into a monoclinic structure with space group $P2_1/n$ (No. 14).

Fig. 2(a)–(c) presented the surface SEM images of $BaMgP_2O_7$ ceramics sintered at different temperatures. At 825 °C, a porous microstructure with grain size of 1–4 μm was observed. With increasing temperature to 850 °C, the grain boundary were observed. The majority of the grains had an average size of 1–4 μm. When the temperature reached 925 °C, abnormal grain growth occurred and heterogeneous grain size as large as ~30 μm was observed. Fig. 2(d) presented the energy dispersive spectroscopy (EDS) analysis of the $BaMgP_2O_7$ ceramics. The EDS analysis gave an atomic ratio of 1:0.84:1.88:6.22 for Ba:Mg:P:O, which was close to the ideal value of 1:1:2:7.

Fig. 3 presented the apparent and relative densities of $BaMgP_2O_7$ ceramic as a function of sintering temperature. It can be observed that with the increase of the sintering temperature the relative density firstly increased with the elimination of the pores and reached a maximum of 96.8% at 850 °C. The relative density decreased slightly with the further increase of sintering temperature, which might be due to over-burning and abnormal grain growth. The high relative density indicated $BaMgP_2O_7$ was easy to be densified.

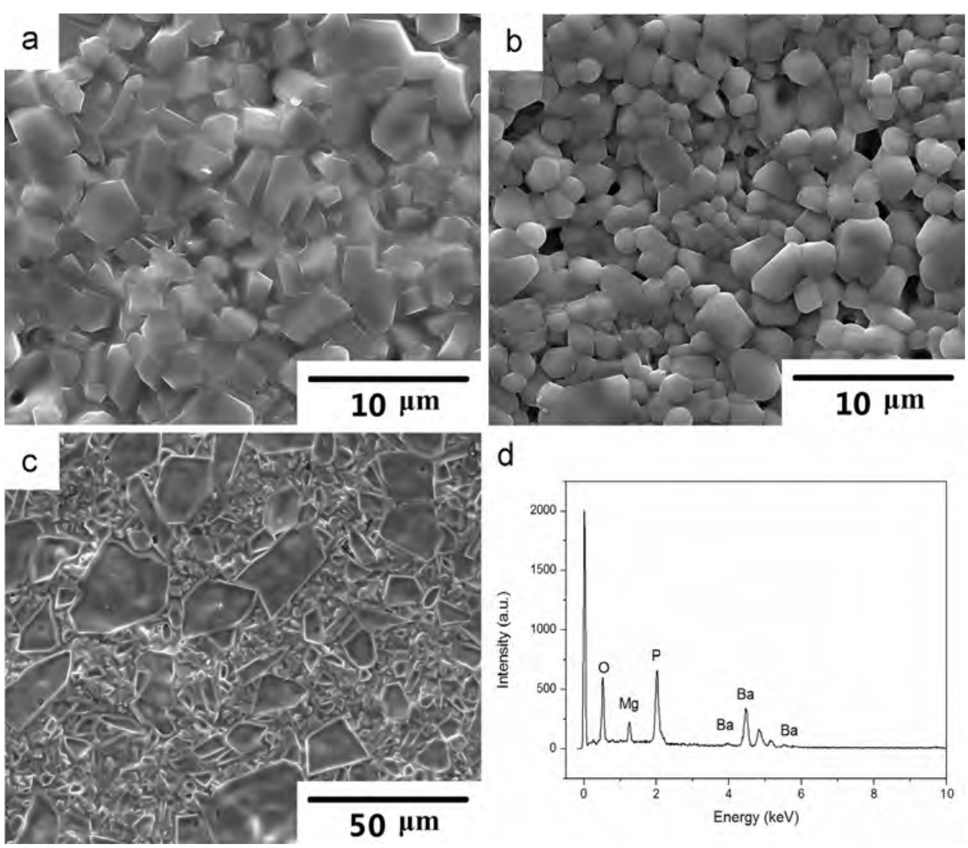

Fig. 2. SEM images of the $BaMgP_2O_7$ ceramics sintered at (a) 825 °C/2 h, (b) 850 °C/2 h, (c) 925 °C/2 h, (d) EDS spectra at 850 °C.

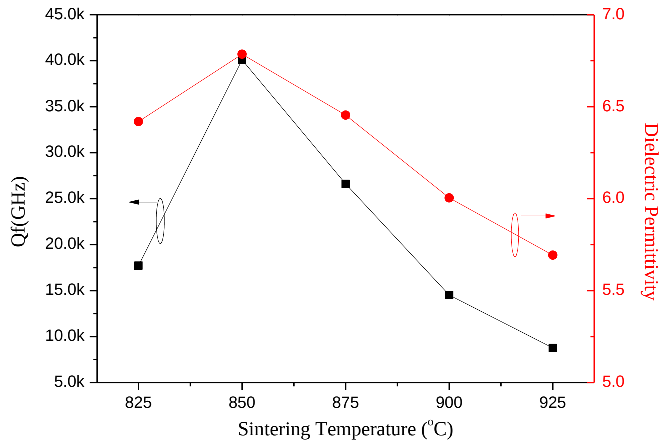

Fig. 4. Microwave dielectric characteristics of $BaMgP_2O_7$ ceramic as functions of sintering temperature.

According to Fan et al. [17], both the permittivity and quality factor can be simultaneously measured with a high accuracy by the shielded cavity method. Fig. 4 illustrated the microwave relative dielectric permittivities and $Q\times f$ values of ceramics as a function of sintering temperature. As the sintering temperature increased, the permittivity firstly increased and then reached a maximum value of 6.8 at the optimum sintering temperature of 850 °C. In general the dielectric constant in microwave frequency was dependent on the density, sencondary phases, and the crystal structure. The higher density led to a greater dielectric constant. In addition the highest quality factor was observed for the highest densification. The ceramic of $BaMgP_2O_7$ sintered at 850 °C presented an optimum $Q\times f$ value of 40,089 GHz (at 11.7 GHz) with a TCF value of −40.6 ppm/°C calculated from Eq. (1). The $Q\times f$ value of microwave dielectric ceramic was determined by the intrinsic loss and extrinsic loss. The intrinsic loss was depend on lattice vibrational modes and the extrinsic loss was influenced by many defects, such as pore, density, second phases, grain sizes, and impurities [18–20]. The reason that the $Q\times f$ decreased with the sintering temperature might be attributed to the rapid grain growth of $BaMgP_2O_7$ as observed in Fig. 2(c).

4. Conclusions

The ceramics of $BaMgP_2O_7$ were synthesized by solid-state reaction method. The ceramics could well sintered at low temperature of 850 °C. $BaMgP_2O_7$ ceramic sintered at 850 °C for 2 h exhibited good microwave dielectric properties of $\varepsilon_r=6.8$, $Q\times f=40{,}089$ GHz (@11.7 GHz), and $\tau_f=-40.6$ ppm/°C. This material had a low permittivity, high quality factor, and medium negative τ_f values, which might be an attractive candidate of microwave substrate.

Acknowledgments

This work was supported by Shaanxi Provincial Natural Science Fund under Grant no. 2014JM2-5056.

References

[1] S.P. Wu, D.F. Chen, C. Jiang, Y.X. Mei, Q. Ma, Synthesis of monoclinic $CaSnSiO_5$ ceramics and their microwave dielectric properties, Mater. Lett. 91 (2013) 239–241.

[2] C.X. Su, L. Fang, Z.H. Wei, X.J. Kuang, H. Zhang, $LiCa_3ZnV_3O_{12}$: a novel low-firing, high Q microwave dielectric ceramic, Ceram. Int. 40 (2014) 5015–5018.

[3] H.F. Zhou, F. He, X.L. Chen, J. Chen, L. Fang, W. Wang, X.B. Miao, A novel thermally stable low-firing $LiMg_4V_3O_{12}$ ceramic: sintering characteristic, crystal structure and microwave dielectric properties, Ceram. Int. 40 (2014) 6335–6338.

[4] L. Fang, Z.H. Wei, C.X. Su, F. Xiang, H. Zhang, Novel low-firing microwave dielectric ceramics: $BaMV_2O_7$ (M=Mg, Zn), Ceram. Int. 40 (2014) 16835–16839.

[5] R. Umemura, H. Ogawa, H. Ohsato, A. Kan, A. Yokoi, Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2$ ceramic, J. Eur. Ceram. Soc. 25 (2005) 2865–2870.

[6] X.W. Jiang, C.C. Li, C.X. Su, Z.H. Wei, L. Fang, Low temperature firing and microwave dielectric properties of $BaCaV_2O_7$ ceramics, Ceram. Int. 41 (2015) 5172–5176.

[7] L. Fang, F. Xiang, C.X. Su, H. Zhang, A novel low firing microwave dielectric ceramic $NaCa_2Mg_2V_3O_{12}$, Ceram. Int. 39 (2013) 9779–9783.

[8] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, Int. Mater. Rev. 53 (2008) 57–90.

[9] J.J. Bian, D.W. Kim, K.S. Hong, Glass-free LTCC microwave dielectric ceramics, Mater. Res. Bull. 40 (2005) 2120–2129.

[10] J.J. Bian, D.W. Kim, K.S. Hong, Microwave dielectric properties of $A_2P_2O_7$ (A=Ca, Sr, Ba; Mg, Zn, Mn), Jpn. J. Appl. Phys. 43 (2004) 3521–3525.

[11] J.J. Bian, D.W. Kim, K.S. Hong, Microwave dielectric properties of $Ca_2P_2O_7$, J. Eur. Ceram. Soc. 23 (2003) 2589–2592.

[12] T. Guo, W.J. Wu, Y.L. Wang, Y.X. Li, Relations on synthesis, crystal structure and microwave dielectric properties of $SrZnP_2O_7$ ceramics, Ceram. Int. 38S (2012) S187–S190.

[13] J.J. Bian, D.W. Kim, K.S. Hong, Microwave dielectric properties of $(Ca_{1-x}Zn_x)_2P_2O_7$, Mater. Lett. 59 (2005) 257–260.

[14] Y.K. Kim, S.H. Choi, H.K. Jung, Photoluminescence properties of Eu^{2+} and Mn^{2+}-activated $BaMgP_2O_7$ as a potential red phosphor for white-emission, J. Lumin. 130 (2010) 60–64.

[15] R.F. Wang, L.Y. Zhou, Y.L. Wang, Luminescent properties of $MMgP_2O_7$:Eu^{3+} (M=Ca, Sr, Ba) phosphor, J. Rare Earth 29 (2011) 1045–1048.

[16] M. Serghini Idrissi, L. Rghioui, R. Nejjar, L. Benarafa, M. Saidildrissi, A. Lorriaux, F. Wallart, Spectres de vibration des diphosphates monocliniques de formule AMP_2O_7, Spectrochim. Acta A 60 (2004) 2043–2052.

[17] X.C. Fan, X.M. Chen, X.Q. Liu, Complex-permittivity measurement on high-Q materials via combined numerical approaches, IEEE Trans. Microw. Theory 53 (2005) 3130–3134.

[18] D. Zhou, L.X. Pang, X. Yao, H. Wang, Influence of sintering process on the microwave dielectric properties of $Bi(V_{0.008}Nb_{0.992})O_4$ceramics, Mater. Chem. Phys. 115 (2009) 126–131.

[19] S. George, M.T. Sebastian, Synthesis and microwave dielectric properties of novel temperature stable high Q, $Li_2ATi_3O_8$ (A=Mg, Zn) ceramics, J. Am. Ceram. Soc. 93 (2010) 2164–2166.

[20] H. Tamura, Microwave loss quality of $(Zr_{0.8}Sn_{0.2})TiO_4$, Am. Ceram. Soc. Bull. 73 (1994) 92–95.